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HYBRID EXCHANGE CORRELATION FUNCTIONALS AND POTENTIALS: CONCEPT ELABORATION

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This paper deals with hybrid functionals that contain exact exchange energy and are the most popular and effective functionals in modern density functional theory. Emphasis is laid on generalization of the notion of a “hybrid functional,” which arises from the introduction of the spatial dependence of the exact exchange admixture (local hybrid functionals). Problems inherent in hybrid functionals are considered along with problems inherent in a wider class of so-called orbital-dependent functionals. In particular, the technique for constructing the local and multiplicative potentials, including the optimized effective potential method, is considered in detail. The theoretical approaches under study are illustrated by calculations of atomization molecular energies and magnetic resonance parameters.

Keywords: density functional theory, hybrid functional, local hybrid functional, localized local hybrid potential, optimized effective potential method, atomization energy, chemical screening constant, g tensor.

INTRODUCTION

Over the past decade or two, density functional theory (DFT) has become one of the most popular methods of electronic structure calculations of atoms, molecules, clusters, solids, etc. [1, 2]. The growing popularity of DFT is primarily determined by the combination of high accuracy, occasionally exceeding the accuracy of strict many-particle methods, and rather moderate requirements to computational resources, which today allow calculations for large systems of interest in nanotechnology, namely, biologically active molecules containing hundreds of atoms, etc.

Modern DFT is based on two Hohenberg–Kohn’s theorems [3]. The first theorem sets one-to-one correspondence between the electron density of a many-electron system in the ground state and the “external” potential, i.e., the electrostatic potential of nuclei, which are immobile within the framework of the adiabatic approximation, and the external static electric field. The second Hohenberg–Kohn theorem is essentially the variational principle formulated in terms of electron density as a basic quantity. In contrast to the many-electron wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N)$ (where $\mathbf{r}_i = (x_i, y_i, z_i)$ are the spatial coordinates of an electron with the index i ; σ_i is its spin variable; and N is the number of electrons in the system), including a lot of redundant information, the electron density

$$\rho(\mathbf{r}_1) = N \int \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N) \Psi^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \sigma_1, \sigma_2, \dots, \sigma_N) d\mathbf{r}_2 \dots d\mathbf{r}_N d\sigma_1 \dots d\sigma_N \quad (1)$$

is primarily attractive because it is easily perceivable (corresponds to the intuitive concepts of the electronic structure of atoms, molecules, etc.) and relatively simple from mathematical viewpoint (determined by a triplet of spatial variables).

From the viewpoint of practical calculations, however, the situation is much more problematic. Regrettably, an

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equation similar to the Schrödinger equation with electron density instead of the many-electron wave function has not yet been formulated. The major difficulty lies in impossibility of expressing the kinetic energy of the system with an acceptable accuracy in terms of density alone (the fundamental Thomas–Fermi model [4, 5] failed to provide an accuracy needed for real chemical applications). The Kohn–Sham formalism proved to be a solution to this problem [6]. In this formalism, an imaginary many-electron system is introduced which has the same electron density distribution as the real system in question, but differs from it in the absence of interelectron interaction. This fictitious “noninteracting” system is described by a single-determinantal wave function composed of the (Kohn–Sham) one-electron orbitals $\{\varphi_i(\mathbf{r})\}_{i=1}^{N_{\text{occ}}}$ (N_{occ} is the number of occupied spatial orbitals among which there may be recurrent doubly occupied orbitals) with which the total electron energy of a *real* system can be recorded as

$$E = -\frac{1}{2} \sum_{i=1}^{N_{\text{occ}}} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) d\mathbf{r} - \sum_K Z_K \int \frac{\rho(\mathbf{r})}{|\mathbf{r} - \mathbf{R}_K|} d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[\rho] = T_s \{\varphi_i(\mathbf{r})\}_{i=1}^{N_{\text{occ}}} + V_{ne}[\rho] + J[\rho] + E_{\text{xc}}[\rho], \quad (2)$$

where Z_K is the charge on an (immobile) nucleus with the index K , and \mathbf{R}_K are the spatial coordinates of this nucleus; the electron density is defined as

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_{\text{occ}}} |\varphi_i(\mathbf{r})|^2. \quad (3)$$

In the right part of (2), the first term, T_s , describes the kinetic energy of a *noninteracting* system; the second term, V_{ne} , is the attraction of electrons to nuclei; and J is the classic contribution of electron repulsion to the energy. Finally, E_{xc} , which is called an *exchange correlation functional*, is the residue of the electron energy of the real system, namely, the “nonclassic” contribution of interelectron interaction to the potential energy and the difference between the kinetic energies of the real and imaginary systems:

$$E_{\text{xc}} = (V_{ee} - J) + (T - T_s). \quad (4)$$

DFT is an essentially strict theory provided that an *exact exchange correlation functional* is known. Regretfully, an “ideal” functional of this kind is inaccessible; construction of increasingly exact approximations to E_{xc} remains the central problem of modern density functional theory. The exchange correlation functional is virtually “the core of DFT” because it eventually affects the predictive strength and efficiency of the theory.

This work does not claim to give a full description of the evolution of the exchange correlation functionals. Instead we attempt to trace the origin of so-called *hybrid* functionals and prospects for their development because these are now the most popular and effective functionals. We also try to understand reasons for their success and to demonstrate several pitfalls in their realization, which often escape the attention of researchers. This work deals with problems inherent in hybrid functionals and *orbital-dependent* functionals, which have recently become reliable tools of applied DFT; in particular, this work considers in detail the technique for constructing the local and multiplicative potentials, including the optimized effective potential method and its approximate versions. To avoid cumbersome equations we give all relations for the case of *real* orbitals, response functions, etc. (which can be readily generalized to complex objects). Here we consider only finite systems (atoms, molecules, clusters, etc.).

LOCAL AND SEMILOCAL DENSITY FUNCTIONALS

Before describing the density functionals it is necessary to introduce several additional definitions. The *spin* density functional theory (SDFT) is a natural generalization of DFT for describing open-shell systems or any systems in an external magnetic field. In this theory, the exchange-correlation energy is defined by two variables, namely, by electron densities with spins α (ρ_α) and β (ρ_β):

$$E_{\text{xc}} = E_{\text{xc}}[\rho_\alpha; \rho_\beta], \quad (5)$$

where*

$$\rho_{\sigma}(\mathbf{r}) = \sum_{i_{\sigma}=1}^{N_{\sigma,\text{occ}}} |\varphi_{i_{\sigma}}(\mathbf{r})|^2, \quad \sigma = \alpha, \beta; \quad (6)$$

$$\rho_{\alpha}(\mathbf{r}) + \rho_{\beta}(\mathbf{r}) = \rho(\mathbf{r}). \quad (10)$$

The introduction of dimensionless *spin polarization* ζ is an alternative method for including spin effects in calculations:

$$\zeta(\mathbf{r}) = \frac{\rho_{\alpha}(\mathbf{r}) - \rho_{\beta}(\mathbf{r})}{\rho(\mathbf{r})}. \quad (8)$$

It can easily be seen that the pair of variables $(\rho_{\alpha}; \rho_{\beta})$ is quite equivalent to the pair $(\rho; \zeta)$. Naturally, in closed-shell systems, $\rho_{\alpha} = \rho_{\beta} = \rho/2$ (or $\zeta = 0$) at each point of space.

Using the variational principle for energy functional (2) and imposing an additional condition of orthonormal orbitals yields Kohn–Sham one-electron equations (similar in form to Hartree–Fock equations [7]):

$$\left[-\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (9)$$

where

$$v_s(\mathbf{r}) = -\sum_K \frac{Z_K}{|\mathbf{r} - \mathbf{R}_K|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (10)$$

is the Kohn–Sham potential, and

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta \rho(\mathbf{r})} \quad (11)$$

is the exchange correlation potential defined as a functional derivative [8] of the exchange correlation functional with respect to density**.

In the *local density approximation* (LDA) [9-13], which has recently been widely used for a long time, the exchange correlation functional was recorded as an integral of a certain function of spatial variables. The latter, in turn, is only determined by electron density (and spin polarization) at a given point:

$$E_{xc}^{\text{LDA}} = \int \varepsilon_{xc}^{\text{LDA}}[\rho_{\alpha}(\mathbf{r}); \rho_{\beta}(\mathbf{r})] d\mathbf{r} = \int e_{xc}^{\text{LDA}}[\rho_{\alpha}(\mathbf{r}); \rho_{\beta}(\mathbf{r})] \rho(\mathbf{r}) d\mathbf{r}. \quad (12)$$

The integrand functions $\varepsilon_{xc}^{\text{LDA}}$ and e_{xc}^{LDA} are two alternative definitions of the exchange correlation energy density (e_{xc}^{LDA} is often called, more explicitly, energy density per electron); here we use the first definition ($\varepsilon_{xc}^{\text{LDA}}$).

LDA naturally appeared in electron gas theory (see, e.g., [14]) and proved a very effective method for describing solids as three-dimensional periodic systems. On the other hand, LDA is a rather rough approximation for describing finite objects (atoms and molecules), whose electron density distribution has almost nothing in common with that in a homogeneous electron gas. Before starting to discuss more exact methods, it should be noted that it is common practice to divide all exchange correlation functionals into groups of “exchange” and “correlation” functionals:

$$E_{xc} = E_x + E_c, \quad (13)$$

and model each contribution separately. Strictly speaking, this division is rather conventional and even partly equivocal [15] and is dictated mainly by practical considerations of convenience (for discussion, see the next section). Nevertheless, based

*The density ρ_{σ} can also be obtained directly from (1) if integration (summation) over the spin variable σ_1 is not carried out.

**For open-shell systems described within the spin-unrestricted Kohn–Sham method, two coupled-perturbed equations appear instead of one equation (9): one for spin α , and the other, for spin β , which accordingly include different spin-dependent exchange correlation potentials $v_{xc,\alpha} \neq v_{xc,\beta}$.

on the known expansion in a series of the reciprocal powers of the Seitz radius $r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$ for the homogeneous electron gas energy (see Eq. (3.37) from [14]) in LDA one can naturally determine the local exchange energy (often called “Slater exchange” [10] and designated as E_x^S , although it was suggested by Dirac [9]), which is attractive in having a very simple expression:

$$E_x^{\text{LDA}} \equiv E_x^S = \sum_{\sigma=\alpha,\beta} E_{x,\sigma}^{\text{LDA}} = \sum_{\sigma=\alpha,\beta} \int \varepsilon_{x,\sigma}^{\text{LDA}}[\rho_\sigma(\mathbf{r})]d\mathbf{r}, \quad (14)$$

where

$$\varepsilon_{x,\sigma}^{\text{LDA}} = -C_x \rho_\sigma^{4/3}(\mathbf{r}), \quad C_x = \frac{3}{2} \left(\frac{3}{4\pi}\right)^{1/3} = 0.9305257\dots \quad (15)$$

In contrast to E_x , the correlation energy E_c of a homogeneous electron gas [11-14] cannot be reproduced in analytical form. The most popular parametrizations of E_c , VWN* [12] and PW91 [13], are constructed by analytically interpolating the results of Monte Carlo stochastic simulation of electron correlation [16].

Since the mid-1980s, DFT became even more popular as a quantum chemical-method because of the appearance of the *generalized gradient approximation* (GGA) [17-20], which substantially increased the accuracy of description. In the GGA, the exchange correlation functional includes not only electron density, but also information about its inhomogeneity in the form of the absolute value of the density gradient:

$$E_{xc}^{\text{GGA}} = \int \varepsilon_{xc}^{\text{GGA}}[\rho_\alpha(\mathbf{r}), |\nabla\rho_\alpha(\mathbf{r})|; \rho_\beta(\mathbf{r}), |\nabla\rho_\beta(\mathbf{r})|]d\mathbf{r}. \quad (16)$$

More recently, a number of new GGA functionals were created and allowed higher accuracy of calculations of definite properties of molecular systems** [21-25]. Within the framework of the GGA, the most popular functionals are Becke’s exchange functional (B88) [20], Handy–Cohen’s “optimized exchange” [26]; Lee–Yang–Parr’s (LYP) [21, 22] and Perdew–Wang’s correlation functionals (PW91) [13, 23, 24], and Perdew–Burke–Ernzerhof’s (PBE) exchange correlation functional [25].

Further development of the exchange correlation functionals followed two main trends: inclusion of the new inhomogeneity parameters of electron density or addition of the exact (Hartree–Fock) exchange energy. The first direction was called “meta-GGA” (or MGGA) [27-35] and used, along with the density gradient, the Laplacian of density $\nabla^2\rho$ and/or the *positively defined local density of kinetic energy* τ ***

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_{i_\sigma=1}^{N_{\sigma,\text{occ}}} |\nabla\varphi_{i_\sigma}(\mathbf{r})|^2, \quad \sigma = \alpha, \beta. \quad (17)$$

Thus, the meta-GGA functional can be recorded in general form as

$$E_{xc}^{\text{MGGA}} = \int \varepsilon_{xc}^{\text{MGGA}}[\rho_\alpha(\mathbf{r}), |\nabla\rho_\alpha(\mathbf{r})|, \nabla^2\rho_\alpha(\mathbf{r}), \tau_\alpha(\mathbf{r}); \rho_\beta(\mathbf{r}), |\nabla\rho_\beta(\mathbf{r})|, \nabla^2\rho_\beta(\mathbf{r}), \tau_\beta(\mathbf{r})]d\mathbf{r}. \quad (18)$$

*As a matter of fact, there are two versions of the VWN parametrization: the “standard” VWN-5 parametrization, recommended for use in the original work, and VWN-3, which is used more rarely.

**The accuracy of calculation of various properties (atomization energies of molecules in the equilibrium state, barriers of reactions, geometrical parameters, vibrational frequencies, optical properties, magnetic resonance parameters, etc.) generally differs substantially between functionals. Therefore, preference should be given to the functional that yields the highest accuracy of calculation for the property.

***The phrase “positively defined” is needed in view of the fact that any energy density in general and the kinetic energy density in particular are *basically ambiguous*. For example, identical results will evidently be provided by integration

over the entire space of the expression $\frac{\lambda}{2} \sum_{i_\sigma=1}^{N_{\sigma,\text{occ}}} |\nabla\varphi_{i_\sigma}(\mathbf{r})|^2 - \frac{(1-\lambda)}{2} \sum_{i_\sigma=1}^{N_{\sigma,\text{occ}}} \varphi_{i_\sigma}^*(\mathbf{r})\nabla^2\varphi_{i_\sigma}(\mathbf{r})$ for any value of the parameter λ (see below).

From practical viewpoint, today the Tao–Perdew–Staroverov–Scuseria (TPSS) functional is the most effective functional from this class [35].

The second trend, namely, addition of exact exchange led to the creation of especially effective hybrid functionals, which are considered in the next section of this paper.

The LDA, GGA, and meta-GGA functionals are generally classified as “semilocal”; the density of exchange correlation energy in them is given in terms of the function that depends, at each point of space, on the value of electron density and its derivatives (and also, possibly, on τ (17)) obtained *exclusively* for that point (Eq. (18)). In other words, in contrast to the *essentially nonlocal* exact exchange (see below), the semilocal ϵ_{xc} *contains no* integration over the other independent set of spatial coordinates.

Finally, it is worth mentioning that direct modeling of exchange correlation *potentials* avoiding the stage of energy functionals is possible [36-40]. *Model* potentials of this kind are constructed based on the principle of their correct behavior both in the infinitely remote (asymptotic) region and in the (sub)valent and core regions. This makes it possible to reproduce, with a high degree of accuracy, “responsive” molecular properties such as the vertical excitation energy, dipole polarizability and hyperpolarizability, vertical ionization potential, and electron affinity. The major disadvantages of this approach are limited generality and applicability; since the energy functional is unknown, the total energy and hence the thermochemical properties of molecular systems cannot be obtained with these potentials.

TRADITIONAL (“GLOBAL”) HYBRID FUNCTIONALS

It is widely known that the exchange energy of electrons with the same spin (or so-called “Fermi correlation,” which is a direct consequence of the Pauli principle) is the predominant contribution to the total exchange correlation energy (85-95% of the latter). Therefore, it would be reasonable to expect good results if the rough semilocal exchange functional is replaced with an exact (Hartree–Fock) equation for exchange energy,

$$E_x^{\text{exact}} = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{i_\sigma, j_\sigma}^{\text{occ}} \iint \frac{\varphi_{i_\sigma}(\mathbf{r})\varphi_{j_\sigma}(\mathbf{r})\varphi_{i_\sigma}(\mathbf{r}')\varphi_{j_\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (19)$$

and further modeled with the density functionals relative to the small “residue,” i.e., Coulomb correlation energy E_c (Eq. (13))*.

It should be emphasized that exact exchange (19) has a number of advantages over any semilocal exchange functional; the major advantage is total elimination of the absurd, nonphysical “self-interaction.” This effect can readily be understood from (2): for one-electron systems (for example, for the hydrogen atom or H_2^+ molecular ion) the classical electron repulsion energy $J(\rho)$ should be completely compensated by the exchange correlation energy E_{xc} (in other words, the “delocalized” position of an electron cannot be interpreted in the static sense because the electron cannot experience electrostatic repulsion from itself lying at a different point of space at a different moment of time!). As a matter of fact, in any of the semilocal exchange functionals mentioned in the previous section, self-interaction is compensated only partially**. The presence of self-interaction is also detrimental to description of many-electron systems, and especially to description of nonthermochemical properties that are sensitive to the subtle features of electron density distribution [41, 42]. Elimination of self-interaction by explicitly subtracting it [43] is quite effective [44], but has one important drawback, namely, the scheme of [43] *is not invariant* under the unitary transformations of the occupied one-electron orbitals.

The ability of exact exchange (19) to fully compensate self-interaction follows from its definition. This property can also directly provide a regular asymptotic behavior of the corresponding exchange correlation potentials, which is especially

*Here and below, summation over occupied orbitals is designated for brevity as “occ” (occupied).

**Self-interaction can be eliminated from the *correlation* functionals (“self-correlation”) much more easily, which was achieved in several functionals [33-35] using the kinetic energy density τ (Eq. (17)).

important for correct description of a number of properties calculated within the framework of linear response theory and/or second order perturbation theory (polarizability, magnetic resonance parameters, etc.).

Regretfully, with all positive features of exact exchange, attempts to construct an exchange correlation functional in the form of

$$E_{xc} = E_x^{\text{exact}} + E_c, \quad (20)$$

proved inapplicable to description of chemical bonds in molecules [45] and gave acceptable results only for one-center systems (atoms, ions) [46-48]. This situation can be explained in the following way. In DFT, the (Coulomb) correlation energy, modeled with the correlation functionals E_c , is generally implied to be only its *dynamic* (short-range) component E_c^d , which is responsible for lower probability of situations in which electrons with opposite spins approach one another to short distances*. Another type of correlation is *nondynamic* (long-range) correlation, which is especially pronounced in description of homolytic dissociation of molecules. Let us consider the simple two-electron case, namely, the dissociated H_2 molecule. There are two interpretations of the nondynamic correlation: one pertains to *real* space and the other, to Hilbert space. In the first interpretation, the energy gain E_c^{nd} arises from further decrease in Coulomb repulsion of electrons due to the higher probability of occurrence of one electron near, say, the “right” nucleus (if the dissociated molecule is considered to be orientated “horizontally”) provided that another electron lies near the “left” nucleus**. In *Hilbert* space of many-electron wave functions, the one-configuration ($1\sigma_g^2$) description of an “extended” H_2 molecule is evidently inadequate; the contribution of the excited configuration $1\sigma_u^2$ to the exact wave function increases with the internuclear distance (in the limit of complete dissociation, the $1\sigma_g^2$ and $1\sigma_u^2$ configurations become degenerate, and their contributions become identical). Thus, the decreased energy E_c^{nd} can be interpreted as admixing of the low-lying excited configurations. This effect is obviously expected not only for dissociated molecules, but also for many transition metal compounds, where the effects of quasidegeneration are especially pronounced.

By definition, exact exchange (19) includes only the Fermi electron correlation with identical spins, and hence (20) has no nondynamic Coulomb correlation. It is important to emphasize that exact exchange is *essentially nonlocal*. This becomes quite evident if we rewrite (19) to obtain an equation that resembles (12), (14), (16), and (18):

$$E_x^{\text{exact}} = \sum_{\sigma=\alpha,\beta} E_{x,\sigma}^{\text{exact}} = \sum_{\sigma=\alpha,\beta} \int \varepsilon_{x,\sigma}^{\text{exact}}(\mathbf{r}) d\mathbf{r}, \quad (21)$$

where

$$\varepsilon_x^{\text{exact}}(\mathbf{r}) = -\frac{1}{2} \sum_{i_\sigma, j_\sigma}^{\text{occ}} \varphi_{i_\sigma}(\mathbf{r}) \varphi_{j_\sigma}(\mathbf{r}) \int \frac{\varphi_{i_\sigma}(\mathbf{r}') \varphi_{j_\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (22)$$

is the exact exchange energy density. A comparison of Eq. (22) with Eqs. (14), (16), and (18) shows that these equations are quite different. In contrast to the exchange energy density in LDA, GGA, or meta-GGA, the exact exchange energy density at each point of space conveys information (integrated over the second independent set of spatial variables (\mathbf{r}')) about the behavior of the one-electron orbitals *over entire real space*.

As opposed to the case of exact exchange E_x^{exact} , the semilocal exchange functionals (denoted for brevity as E_x^{DFT} , where DFT = LDA, GGA, MGGGA) can *effectively* take into account nondynamic correlation. Therefore, (13) can be conventionally rewritten as [26, 49]:

*The *Coulomb* correlation of electrons with identical spins makes a much lower contribution, but is also included in several models (e.g., [27]).

**“Left-right correlation.”

$$E_{xc} = E_x^{\text{DFT}} + E_c^{\text{DFT}} = \left(E_x^{\text{exact}} + E_c^{\text{nd}} \right) + E_c^{\text{DFT}}; \quad (23)$$

in other words, it will be more appropriate to interpret the exchange density functionals as the functionals that describe electron exchange together with nondynamic correlation:

$$E_x^{\text{DFT}} = E_x^{\text{exact}} + E_c^{\text{nd}}. \quad (24)$$

The property of the exchange functionals expressed by (24) follows exactly from the local nature of these functionals (for details of this discussion, see [49]). Also, it should be noted that partitioning (24) is of methodological rather than practical importance because it is difficult to separate exchange from nondynamic correlation *explicitly*.

Summarizing the aforesaid and comparing (20) and (23), one can easily see that the former is free from any nonphysical self-interaction and contains no nondynamic correlations, while the latter contains both. Consequently, a correct choice of a combination of the right parts of (20) and (23) could be a compromise to ensure *balance between the elimination of self-interaction and the inclusion of nondynamic correlation*. The simplest choice is a linear combination, naturally leading to the notion of a *hybrid* exchange correlation functional

$$E_{xc}^{\text{hybr}} = a_0 E_x^{\text{exact}} + (1 - a_0) E_x^{\text{DFT}} + E_c, \quad 0 \leq a_0 \leq 1. \quad (25)$$

In this form (with $E_x^{\text{DFT}} = E_x^{\text{LDA}}$ and $a_0 = 0.5$) the hybrid functional was introduced by Becke in 1993 [50]. He used a different theoretical rationale for the hybrid functional, which was based on the *adiabatic binding* formalism of Kohn–Sham's fictitious system (in which interelectron interaction was absent) with a real system [51].

The hybrid functional based on Becke's three-parameter scheme (B3) became one of the most popular functionals [52]:

$$E_{xc}^{\text{hybr}} = a_0 E_x^{\text{exact}} + (1 - a_0) E_x^{\text{LDA}} + a_x \Delta E_x^{\text{B88}} + E_c^{\text{LDA}} + a_c \Delta E_c^{\text{GGA}}, \quad (26)$$

$$a_0 = 0.2, \quad a_x = 0.72, \quad a_c = 0.81,$$

where ΔE_x^{B88} is the gradient correction to the exchange energy taken from the B88 functional [20], and ΔE_c^{GGA} is the gradient correction to the correlation energy*. The numerical parameters a_0 , a_x , and a_c were obtained by fitting the thermochemical data obtained by using functional (26) to the corresponding experimental data. In [52] for ΔE_c^{GGA} we used ΔE_c^{PW91} [23, 24]. Later it appeared [53] that a combination of the B3 scheme with the LYP correlation functional [21, 22] led to slightly more exact results**. The successful use of B3LYP initiated the development of new hybrid functionals. Of hybrids that appeared recently one can mention the Becke-97 (B97) [54] and Hamprecht–Cohen–Tozer–Handy (HCTH) functionals [55]. The major disadvantage of these functionals is that they are overcrowded with the empirical (fitting) parameters while the accuracy of the description of molecular systems is moderate (e.g., B97 includes 10 parameters, and HCTC includes 15). On the other hand, there were quite opposite attempts such as the PBE0PBE functional [56]. This functional has no fitting parameters, and a functional of the form of (25) is used for which the choice of the value of a_0 was based on certain general theoretical analysis [57]. Nevertheless, the B3LYP three-parameter functional remained the most popular exchange

*In GGA, the exchange (correlation) functional is generally represented as the sum of two terms:

$$E_{xc}^{\text{GGA}} = E_{xc}^{\text{LDA}} + \Delta E_{xc}^{\text{GGA}}.$$

**Strictly speaking, for the LYP correlation functional, there is no *explicit* gradient correction ΔE_c^{LYP} ; therefore, one can use the following artificial method. The correlation energy is formally recorded as $E_c^{\text{LYP}} = E_c^{\text{LDA}} + \Delta E_c^{\text{LYP}}$. After that, in (26) we perform a substitution $a_c \Delta E_c^{\text{LYP}} = a_c (E_c^{\text{LYP}} - E_c^{\text{LDA}})$, where for E_c^{LDA} one can use E_c^{VWN} [12]. The uncontrollable alternative versions in using the two different versions of the VWN parametrization (see footnote * on p. S4) in different quantum-chemical programs are often a source of confusion and irreproducible results obtained by using the B3LYP functional.

correlation functional ever used in DFT for solving physicochemical problems*; this is a good compromise between the small number of empirical fitting parameters and the wide spectrum of properties it describes (with high accuracy).

The hybrid functionals owe much of their success not only to their unique ability to predict thermochemical results and molecular structure, but even, occasionally, to the unique chance they give us in our efforts to obtain acceptable accuracy in calculations of more “delicate” properties that are sensitive to the subtle details of electron density distribution**. These are, e.g., the parameters of nuclear magnetic resonance (NMR) and electronic paramagnetic resonance (EPR) of transition metal complexes. As examples we can cite the iron $\delta(^{57}\text{Fe})$ and ruthenium $\delta(^{103}\text{Ru})$ chemical shifts in the corresponding complex compounds [58, 59], as well as the electronic g tensors of metal complexes from the first transition row [60].

As mentioned above, the hybrid functionals are associated with an undesirable effect of “hyperparametrization.” It appeared that there was a radically different way, leading to generalization of the notion “hybrid functional” analyzed in this work. We emphasize that the traditional hybrid functionals (25) and (26) are called below “global hybrid functionals” (global hybrids for brevity); under “globality” we understand the constancy of the parameter a_0 , which determines the value of exact exchange E_x^{exact} (19).

LOCAL HYBRID FUNCTIONALS

In his pioneering work on hybrid functionals [50], Becke stated that the same energy fraction of exact exchange over the entire real space ($a_0 = 0.5$ and 0.2 in (25) and (26), respectively) could only be regarded as a first approximation. In quantum-chemical calculations, this “first approximation” became widespread practice. Recently, it was suggested that the constancy of the exact exchange admixture should be rejected, which led to the appearance of a new notion — the “local hybrid functional” [61]. In this concept, the exchange correlation functional is recorded as

$$E_{xc}^{\text{loc=hybr}} = \sum_{\sigma=\alpha,\beta} \int \left\{ g_{\sigma}(\mathbf{r}) \varepsilon_{x,\sigma}^{\text{exact}}(\mathbf{r}) + [1 - g_{\sigma}(\mathbf{r})] \varepsilon_{x,\sigma}^{\text{DFT}}(\mathbf{r}) \right\} d\mathbf{r} + E_c^{\text{DFT}}, \quad (27)$$

where $\varepsilon_{x,\sigma}^{\text{exact}}$ is the exact exchange energy density defined in (22). Thus, the exact exchange admixture becomes spatially dependent. The function g_{σ} , which controls the value of this admixture, is called the *local mixing function* (LMF). Evidently, the LMF should satisfy the condition

$$0 \leq g_{\sigma}(\mathbf{r}) \leq 1. \quad (28)$$

In the previous section, balance between the elimination of self-interaction and inclusion of nondynamic correlation was given as one of the reasons for success of the (global) hybrids. Obviously, local hybrid (27) can in principle provide subtler “adjustment” of this balance provided that the choice of LMF is correct and physically determined***. For LMF, the authors of [61] offered the ratio of “Weizsäcker kinetic energy density” τ_w to the local kinetic energy density τ :

$$g_{\sigma}(\mathbf{r}) = \frac{\tau_{w,\sigma}(\mathbf{r})}{\tau_{\sigma}(\mathbf{r})} \equiv \tau_{\sigma}(\mathbf{r}), \quad (29)$$

where

$$\tau_{w,\sigma}(\mathbf{r}) = \frac{1}{8} \frac{|\nabla \rho_{\sigma}(\mathbf{r})|^2}{\rho_{\sigma}(\mathbf{r})}, \quad (30)$$

*Citation of B3LYP amounts to dozens of thousands.

**The total energy of the system is a “too highly integrated” characteristic in this sense; one can easily imagine a situation in which the local variations of density, balanced in a certain way, do not cause any pronounced changes in energy.

***The particular case of the LMF is the constant ($g(\mathbf{r}) = \text{const} = a_0$), which corresponds to the local hybrid (27) degenerated into the global one (25), (26).

and $\tau_\sigma(\mathbf{r})$ is defined by (17). LMF (29) satisfies condition (28); according to the definitions of $\tau_{W,\sigma}$ and τ_σ , it is nonnegative and vanishes at those points at which electron density is locally homogeneous: $\nabla\rho_\sigma = 0$. Then $\tau_{W,\sigma}$ never exceeds τ_σ and becomes equal to it in those regions of space in which the contribution to electron density is due only to one of the occupied orbitals, i.e., where the contribution from the other orbitals is vanishingly small:

$$\rho_\sigma(\mathbf{r}) \cong |\nabla\phi_{k_\sigma}(\mathbf{r})|^2, \quad 1 \leq k \leq N_{\sigma,\text{occ}}. \quad (31)$$

The latter condition is satisfied for the asymptotic region of any molecular system (in this case, $k = N_{\sigma,\text{occ}}$; i.e., the density is determined by only the highest occupied molecular orbital (HOMO)) and, identically, for any system containing *no more than* one electron with spin α and one electron with spin β . Systems of this kind include not only the hydrogen atom or the H_2^+ molecular ion (for which the given situation is desirable because it corresponds to 100 % exact exchange and hence to complete elimination of self-interaction), but also (regretfully) any *two-electron closed-shell system* (e.g., the neutral hydrogen molecule H_2 , helium atom, etc.). Thus, in these two-electron systems, a local hybrid with LMF (29) always degenerates into a global hybrid with $a_0 = 1$.

It was shown [61] that the local hybrid functionals with LMF (29) allow one to obtain quite acceptable results. Good results were obtained for the energy of three-electron bonds in He_2^+ , Ne_2^+ , Ar_2^+ , $(\text{H}_2\text{O})_2^+$, and other symmetrical radical cations and for the barrier height in hydrogen atom transfer reactions, that is, for those properties that cannot be readily reproduced within the framework of DFT with the traditional semilocal functionals or global hybrids. At the same time, the fundamental properties used in computational thermochemistry, namely, the atomization energy of molecules could not be reproduced satisfactorily; for the standard G2-1 set of 55 molecules and radicals [62, 63], the mean absolute deviation from the experimental values was 13-20 kcal/mol (which depended on the ϵ_x^{DFT} and ϵ_c^{DFT} used), but these values exceeded the values obtained, e.g., with BLYP [20-22] and B3LYP [21, 22, 52] functionals several fold.

Recently, we showed [64] that better agreement of atomization energy with experiment was obtained by simply scaling LMF (29),

$$g_\sigma(\mathbf{r}) = \lambda t_\sigma(\mathbf{r}), \quad \lambda < 1. \quad (32)$$

The best results were obtained with $\lambda = 0.48$ when local exchange was combined with the *local* correlation ($\epsilon_x^{\text{DFT}} = \epsilon_x^{\text{LDA}}$ [9, 10], $\epsilon_c^{\text{DFT}} = \epsilon_c^{\text{VWN}}$ [12]). With LMF (32) one could also obtain high accuracy for the barrier heights of reactions [65]. Therefore, this function may be considered a breakthrough in the development of local hybrid functionals (see the ‘‘Brief summary of the results’’ section). The only serious disadvantage of LMF (32) is the loss of the regular asymptotic behavior of the potentials corresponding to the local hybrid functionals of this kind. In the asymptotic region, the exact exchange admixture reached 0.48, but not 1, and elimination of self-interaction, therefore, was incomplete (this leads to worse results in description of the *nonthermochemical* properties calculated with second order perturbation theory or linear response theory). To eliminate this disadvantage we offered a new type of local mixing functions, which differed radically from (29) and (32) [66]. Instead of t_σ (29) we suggested using the *dimensionless gradient* of electron density as a basic variable

$$s_\sigma(\mathbf{r}) = \frac{|\nabla\rho_\sigma(\mathbf{r})|}{2k_F(\mathbf{r})\rho_\sigma(\mathbf{r})} \equiv \frac{|\nabla\rho_\sigma(\mathbf{r})|}{2(3\pi^2)^{1/3}\rho_\sigma^{4/3}(\mathbf{r})} \approx \frac{|\nabla\rho_\sigma(\mathbf{r})|}{6.1873\rho_\sigma^{4/3}(\mathbf{r})}. \quad (33)$$

Based on (33) and exponentially decreasing density of finite systems in the asymptotic region, s_σ changes from zero to infinity; therefore, suitable continuous, monotonous mapping of ray $[0;\infty)$ to a segment $[0;1]$ could be a candidate for LMF. We considered the following functional forms as LMFs: $s^m/(\lambda + s^m)$, $[s/(\lambda + s)]^m$, $[1 - \exp(-\lambda s)]^m$, $[\text{erf}(\lambda s)]^m$, $[\text{th}(\lambda s)]^m$, $[(2/\pi)\text{arc tan}(\lambda s)]^m$, ($m = 1, 2$), etc. ($s = s_\alpha, s_\beta$) with a positive variable λ parameter. All these provide comparable levels of thermochemical accuracy when local exchange is combined with correlation of LYP [21, 22] in functional (27). The best results were obtained for the following choice of LMF [66]:

$$g_\sigma(s_\sigma) = [s_\sigma/(\lambda + s_\sigma)]^2. \quad (34)$$

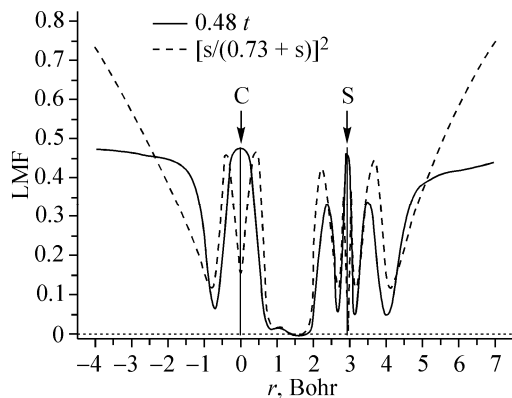


Fig. 1. Local mixing functions (LMF) of two types for the carbon monosulfide molecule (the t and s variables are determined by the conditions of (29) and (33), respectively). Calculation with the LDA functional (S-VWN) in the cc-pVQZ basis. The LMF values correspond to the axis that connects the nuclei.

LMF (34) permits the same level of accuracy as LMF (32) in obtaining atomization energies, and is advantageous in having a regular asymptotic behavior of local hybrids (27) constructed from it.

As an illustration, Fig. 1 shows LMFs of both types for the carbon monosulfide molecule (the calculated values of LMF lie on the axis through the carbon and sulfur nuclei). It can readily be seen that both (t - and s -dependent) LMFs reflect the shell structure of atoms in the molecule, but they do it in qualitatively different ways; t -LMF has a maximum on the nuclei, while s -LMF has a minimum (it is not clear as yet which is preferable). This difference in the asymptotic behavior of the two local mixing functions is evident from Fig. 1.

It should be mentioned that the conceptually local hybrid functional (27) is close to the nondynamic correlation model recently suggested by Becke [67, 68]. For closed-shell systems, the exchange correlation energy functional in the latter formally coincides with (27) (LMF is much more complex in form than (29), (32), or (33)).

Discussing the local hybrid functionals, it should be mentioned that the definition of the exchange energy density is *ambiguous*, which concerns both $\varepsilon_{x,\sigma}^{\text{exact}}$ and $\varepsilon_{x,\sigma}^{\text{DFT}}$ (see footnote *** on p. S4). To any energy density ε ($\int \varepsilon(\mathbf{r}) d\mathbf{r} = E$) one can add a certain “calibrating” function η , whose integral over the entire space is zero; then the function $\tilde{\varepsilon} = \varepsilon + \eta$ can evidently be regarded as the density of the same energy (or one can transform the integral using “three-dimensional integration by parts” and obtain another density equation, see below). A method for constructing an “unambiguous” exchange correlation energy density was offered in [69], but this method is of conceptual rather than practical value. The ambiguity, however, *does not seem* to be a serious obstacle to wide use of the local hybrid functionals (especially in those cases when $\varepsilon_{x,\sigma}^{\text{DFT}}$ is a smooth function $\varepsilon_{x,\sigma}^{\text{LDA}}$ (15)) and can be reformulated as the problem of selecting an appropriate LMF; but this requires strict definition of the exchange energy density, which should be followed in all constructions.

The discussion above implicitly implied self-consistent solutions of (9) and (10) with the exchange correlation potential defined by (11). As will be shown below, derivation of potential (11) is often a serious (technical and conceptual) problem; therefore, “non-self-consistent” calculation of the total energies is common practice in preliminary evaluation of the quality of the new exchange correlation functionals of different types (16), (18), (25), (27). Density is substituted into Eq. (2), where E_{xc} is the functional of interest to us, and, if necessary, we also substitute into this equation the individual orbitals obtained in self-consistent calculation (9) with a potential corresponding to any other functional that is “simpler” from the viewpoint of calculating the functional derivative such as LDA (14), (15). “Non-self-consistent” calculations of this kind,

which may be called “post-LDA” in this case, certainly give lower accuracy. However, their precision is high enough to obtain the general idea about the “thermochemical advantages” of the new functional. This method is applicable only to the total energy calculations; evaluation of any other property requires knowledge of the corresponding potential because the latter remains the only method of conveying the information about this functional, for example, in the form of one-electron orbitals and their energies, which are solutions of (9) later employed in property calculations using perturbation theory. At the same time, derivation of potential (11) is a nontrivial problem every time when the functional involves not only density and its derivatives, but also “orbital-dependent contributions” such as the local density of kinetic energy (17) or exact exchange energy (19) (and/or the density of the latter (22)).

HYBRID FUNCTIONALS WITH DIFFERENT METHODS OF INCLUDING THE SHORT- AND LONG-RANGE COMPONENTS OF INTERELECTRON INTERACTION

In summary of this review of methods for generalizing the notion of “hybrid functional,” we briefly consider an interesting and original method for constructing *exchange* functionals (the correlation component is also considered independently, see above), which is now based on the idea of decomposing the repulsion energy of a pair of electrons (lying at points \mathbf{r} and \mathbf{r}') into the “long-range” (lr) and “short-range” (sr) components [70-75] (range-separated hybrid functionals):

$$E_x = E_x^{\text{lr}} + E_x^{\text{sr}}. \quad (35)$$

The starting point in this method is mathematically very simple; the quantity that is inversely proportional to the interelectron distance is represented as the sum of two complementary contributions:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \frac{\text{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} + \frac{1-\text{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}, \quad (36)$$

where erf is the Gaussian function of error ($\text{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-t^2) dt$), and μ is the numerical fitting parameter. The first

term in the right part of (36) is related to E_x^{lr} from (35), and the second, with E_x^{sr} . The Hartree–Fock (exact exchange) method can be used for E_x^{lr} , and the local density approximation, for $E_x^{\text{sr}*}$. Thus, the long-range contribution to the exchange energy becomes (cf. (21) and (22)):

$$E_x^{\text{lr}} = -\frac{1}{2} \sum_{\sigma=\alpha,\beta} \sum_{i_\sigma, j_\sigma}^{\text{occ}} \iint \frac{\varphi_{i_\sigma}(\mathbf{r})\varphi_{j_\sigma}(\mathbf{r})\text{erf}(\mu|\mathbf{r}-\mathbf{r}'|)\varphi_{i_\sigma}(\mathbf{r}')\varphi_{j_\sigma}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (37)$$

A comparison of Eq. (37) with Eqs. (19), (21), and (22) for exact exchange shows that for $\mu \rightarrow \infty$ the former is reduced to the latter.

In every particular case, explicit equations for the short-range component of exchange energy depend on the type of the approximation used within the framework of DFT (LDA, GGA, etc.). These are generally rather cumbersome equations, which are not specified here. The required information can be found in references cited above in this section. Those references (and also [76]) also give the results of detailed evaluation of the ability of these functionals to reproduce different properties of different physicochemical objects.

*It should be emphasized that this method is evidently beyond the scope of the “hybrid functional” concept; in its original version [70], the long-range component E_x^{lr} was described in terms of the configuration interaction (CI) method.

EXCHANGE CORRELATION POTENTIALS OF THE ORBITAL-DEPENDENT FUNCTIONALS

This section discusses problems of calculating the functional derivatives with respect to density (potentials) (11) of orbital-dependent functionals (for the sake of simplification, the spin index σ is omitted every time when it is insignificant in the current context). Recall the definition of the functional derivative for a certain integrated functional

$$E[\rho] = \int \varepsilon[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}), \nabla^2\rho(\mathbf{r}), \dots, \nabla^n\rho(\mathbf{r})] d\mathbf{r}, \quad (38)$$

where $\rho(\mathbf{r})$ is a certain continuous function of spatial variables. An infinitely small variation of the latter, $\delta\rho(\mathbf{r})$, leads to variation of the functional

$$\delta E_{\rho \rightarrow \rho + \sigma\rho} = E[\rho + \sigma\rho] - E[\rho]. \quad (39)$$

If δE is representable as

$$\delta E_{\rho \rightarrow \rho + \sigma\rho} = \int v(\mathbf{r}) \delta\rho(\mathbf{r}) d\mathbf{r}, \quad (40)$$

then $v(\mathbf{r})$ is called the functional derivative of the E functional with respect to the ρ function:

$$v(\mathbf{r}) \equiv \frac{\delta E}{\delta\rho(\mathbf{r})}. \quad (41)$$

For a composition of functionals, for example, for $E[f[\rho]]$ (E is a functional of f , whose value at each point is, in turn, a functional of ρ) the following equation is valid:

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \int \frac{\delta E}{\delta f(\mathbf{r}')} \frac{\delta f(\mathbf{r}')}{\delta\rho(\mathbf{r})} d\mathbf{r}', \quad (42)$$

which resembles the rule of complex function differentiation and can readily be generalized to complex functionals of any degree of “embeddedness.”

For functional (38), the following is valid*:

$$\frac{\delta E}{\delta\rho(\mathbf{r})} = \left[\frac{\partial \varepsilon}{\partial \rho} \right] (\mathbf{r}) - \left[\nabla \left(\frac{\partial \varepsilon}{\partial \nabla \rho} \right) \right] (\mathbf{r}) + \left[\nabla^2 \left(\frac{\partial \varepsilon}{\partial \nabla^2 \rho} \right) \right] (\mathbf{r}) - \dots + (-1)^n \left[\nabla^n \left(\frac{\partial \varepsilon}{\partial \nabla^n \rho} \right) \right] (\mathbf{r}). \quad (43)$$

Evidently, for energy functionals LDA (14), (15) and GGA (16), as well as meta-GGA (18), derivation does not present any methodological problems only if the latter functionals do not contain a dependence on the kinetic energy density τ (17). In other words, the exchange correlation potential is accessible in explicit form in all cases when the corresponding functional includes a dependence only on electron density and its derivatives (of any order). For brevity these functionals are called “pure density functionals” and designated by E_x^p ; here, ρ denotes density with its derivatives. Complications arise for τ -dependent meta-GGA and hybrid (both global (25), (26) and local (27)) functionals. This is associated with the presence of contributions from the densities of kinetic energy τ (17) and exact exchange energy E_x^{exact} (19) (exact exchange energy density $\varepsilon_x^{\text{exact}}$ (22)) respectively, or with the presence of both, as in the case of local hybrids with t -dependent LMF (29), (32)). The problem lies in the fact that neither τ nor E_x^{exact} (or $\varepsilon_x^{\text{exact}}$) are *explicit* electron density functionals** (from (17),

*In this scalar equation, we use an abbreviated form of the “vector” record; e.g., the term $\nabla(\partial\varepsilon/\partial\nabla\rho)$ should be interpreted as $\partial(\partial\varepsilon/\partial\rho'_x)/\partial x + \partial(\partial\varepsilon/\partial\rho'_y)/\partial y + \partial(\partial\varepsilon/\partial\rho'_z)/\partial z$, where $\rho'_u = \partial\rho/\partial u$, $u = x, y, z$.

**According to the first Hohenberg–Kohn theorem [3], any quantity can be considered a density functional, including a certain Kohn–Sham orbital at an arbitrary point of space. Regretfully, this theorem does not contain any indications on the construction of an explicit (analytical) form of this functional.

(19), and (22) it can readily be seen that the dependence of these functions on the Kohn–Sham orbitals $\{\varphi_i(\mathbf{r})\}_{i=1}^{N_{\text{occ}}}$ or their derivatives can never be reduced to the dependence on density or its derivatives). In the literature, the τ -dependent and hybrid functionals are called “orbital-dependent” functionals (here we use for them the general notation $E_{\text{xc}}^{\text{orb}}$). Incidentally, from formal viewpoint, even equations for the total electron energy in terms of many-particle perturbation theory (e.g., second order Möller–Plesset theory MP2 [7]) can be assigned to orbital-dependent functionals; in this case, however, the energy functional includes not only occupied, but also vacant orbitals (so-called *ab initio* density functionals) [77-80]. Evidently, from any orbital-dependent functional one can always obtain its *functional derivative with respect to* the Kohn–Sham orbitals (FDO) $\delta E_{\text{xc}}^{\text{orb}} / \delta \varphi_i$.

Let us first consider the FDO of pure density functionals. Taking into account the explicit density equation in terms of orbitals (2) and the fact that $v_{\text{xc}}^{\rho} \equiv \delta E_{\text{xc}}^{\rho} / \delta \rho$ is defined *explicitly* in terms of (43), one can record

$$\frac{\delta E_{\text{xc}}^{\rho}}{\delta \varphi_i(\mathbf{r})} = 2\varphi_i(\mathbf{r}) \frac{\delta E_{\text{xc}}^{\rho}}{\delta \rho(\mathbf{r})} = 2v_{\text{xc}}^{\rho}(\mathbf{r})\varphi_i(\mathbf{r}). \quad (44)$$

In (44) we emphasize that the potential v_{xc}^{ρ} is multiplicative (the action of the potential on the orbital is reduced to multiplication of the latter on it); consequently, it can be rewritten in the following way:

$$v_{\text{xc}}^{\rho}(\mathbf{r}) = \frac{1}{2\varphi_i(\mathbf{r})} \frac{\delta E_{\text{xc}}^{\rho}}{\delta \varphi_i(\mathbf{r})}. \quad (45)$$

It is interesting to note that (45) is valid for any φ_i occupied orbital, which reflects the known fact that in the Kohn–Sham formalism, the electrons belonging to different orbitals experience the action of the same potential (this seemingly trivial property is not observed, e.g., in the Hartree–Fock method, see below). Thus, in the case of pure density functionals, it makes no difference whether the potential is evaluated with (43) or recalculated from FDO according to (45).

The situation is quite different for orbital-dependent functionals. Let us consider the functionals that include the dependence on the local density of kinetic energy τ (17) (“ τ -dependent” functionals; for these, we use notation $E_{\text{xc}}^{\rho,\tau}$). As shown in [81],

$$\begin{aligned} \frac{\delta E_{\text{xc}}^{\rho,\tau}}{\delta \varphi_i(\mathbf{r})} = & 2 \left\{ \left[\frac{\partial \varepsilon_{\text{xc}}^{\rho,\tau}}{\partial \rho} \right] (\mathbf{r}) - \left[\nabla \left(\frac{\partial \varepsilon_{\text{xc}}^{\rho,\tau}}{\partial \nabla \rho} \right) \right] (\mathbf{r}) + \dots + (-1)^n \left[\nabla^n \left(\frac{\partial \varepsilon}{\partial \nabla^n \rho} \right) \right] (\mathbf{r}) \right\} \varphi_i(\mathbf{r}) - \\ & \left\{ \left[\nabla \frac{d\varepsilon_{\text{xc}}^{\rho,\tau}}{d\tau} \right] (\mathbf{r}) \nabla \varphi_i(\mathbf{r}) - \left[\frac{\partial \varepsilon_{\text{xc}}^{\rho,\tau}}{\partial \tau} \right] (\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r}) \right\} \equiv 2[\hat{v}_{\text{xc}}^{\rho,\tau} \varphi_i](\mathbf{r}). \end{aligned} \quad (46)$$

The first term on the right side of (46) is the familiar multiplicative contribution to FDO (right side of (43)); the other terms (whose origin is associated exclusively with the dependence on τ) contain the differential operators. Thus, FDO (46) is the result of the action of a certain *nonmultiplicative*, but still local operator (or “semilocal” because of the absence of integration over another independent set of spatial variables, see above) on the φ_i orbital. As a result, “extraction” of the multiplicative potential with (45) becomes impossible. However, the mechanical substitution

$$v_{\text{xc}} \varphi_i \leftarrow \frac{1}{2} \frac{\delta E_{\text{xc}}^{\text{orb}}}{\delta \varphi_i} \quad (47)$$

implies a situation in which the electrons that occupy different orbitals travel at different external potentials, which is obviously a departure from the Kohn–Sham formalism (we emphasize that Eqs. (9)-(11) certainly imply that the Kohn–Sham potential $v_{\text{xc}}(\mathbf{r})$ is local and multiplicative).

Finally, let us consider hybrid functionals (beginning with global functionals, e.g., (25)) with a pure density functional as a contribution $(1-a_0)E_x^{\text{DFT}} + E_c$. Evidently, an orbital-dependent contribution, namely, exact exchange (19) will be a source of problems in constructing the corresponding potential. Therefore, an explicit equation for FDO is as follows:

$$\frac{\delta E_{xc}^{\text{hybr}}}{\delta \varphi_i(\mathbf{r})} = 2a_0[\hat{v}_x^{\text{exact}} \varphi_i](\mathbf{r}) + 2[(1-a_0)v_x^{\text{DFT}}(\mathbf{r}) + v_c(\mathbf{r})]\varphi_i(\mathbf{r}) \equiv 2[\hat{v}_{xc}^{\text{hybr}} \varphi_i](\mathbf{r}), \quad (48)$$

where

$$[\hat{v}_x^{\text{exact}} \varphi_i](\mathbf{r}) = -\sum_j^{\text{occ}} \varphi_j(\mathbf{r}) \int \frac{\varphi_j^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'. \quad (49)$$

Equation (49) is a definition of the *exact exchange operator* \hat{v}_x^{exact} , which is *nonmultiplicative* and *nonlocal* (integrated).

Accordingly, the entire $\hat{v}_{xc}^{\text{hybr}}$ operator in (48) is nonlocal and nonmultiplicative. As in the case of the τ -dependent operators, extraction of the Kohn–Sham potential from $\delta E_{xc}^{\text{hybr}} / \delta \varphi_i$ is impossible. It is interesting to note that if in (25) and (48) we set that $a_0 = 1$ and $E_c = 0$ (accordingly, $v_c(\mathbf{r}) \equiv 0$), we obtain exactly the Hartree–Fock method, in which the variational problem is formulated in terms of orbitals, but not electron density. Accordingly, the Hartree–Fock equations

$$\left[-\frac{1}{2}\nabla^2 - \sum_{K=1}^M \frac{Z_K}{|\mathbf{r}-\mathbf{R}_K|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \right] \varphi_i(\mathbf{r}) + [\hat{v}_x^{\text{exact}} \varphi_i](\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad (50)$$

differ from Kohn–Sham equations (9)-(11) primarily in having the nonmultiplicative and nonlocal exact exchange operator \hat{v}_x^{exact} .

It should be emphasized that in most modern standard quantum-chemical programs (e.g., GAUSSIAN-03 [82]) the hybrid potentials are realized as the $\hat{v}_{xc}^{\text{hybr}}$ nonlocal operators. A similar substitution, (47), is almost insignificant to the calculated total energies, while for several nonthermochemical properties, there are considerable complications, qualitatively changing the ultimate solution. For example, in calculations of magnetic resonance parameters such as the nuclear chemical screening constants [83, 84] or electronic g tensors [85], the external magnetic field considered as minor perturbation can give rise to the *corrections to the* \hat{v}_x^{exact} *operator*, which are of the same order as the corrections to orbitals. In other words, in contrast to the local potential (11) and all other contributions to the Kohn–Sham potential (10), the exact exchange operator acquires *linear response* when an external magnetic field is applied (strictly speaking, in magnetic fields, a more general theory including *electron current density* in addition to ρ should be used instead of conventional DFT [86, 87]). As a result, instead of the direct “one-step” application of perturbation theory we have to start an iterative process of solving coupled-perturbed equations (see [83, 84] for details of the discussion). This is undesirable not only because of greater computation times, but also because of the loss of direct correlation between the quality of the self-consistent solution (in the form of orbitals and orbital energies), on the one hand, and the accuracy of the calculated magnetic resonance parameters, on the other, in view of the fact that the outcome of any iterative process is unpredictable.

Let us now consider *practical* chances to avoid the nonlocal and/or nonmultiplicative contributions to the exchange correlation potential, i.e., to the problem of functional differentiation of the orbital-dependent functional with respect to density. Since the $\delta E_{xc}^{\text{orb}} / \delta \varphi_i$ FDO is accessible and taking into account equation (42), one can formally record the functional derivative $\delta E_{xc}^{\text{orb}} / \delta \rho$ as follows:

$$v_{xc}^{\text{orb}}(\mathbf{r}) = \frac{\delta E_{xc}^{\text{orb}}}{\delta \rho(\mathbf{r})} = \sum_i^{\text{occ}} \int \frac{\delta E_{xc}^{\text{orb}}}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}'. \quad (51)$$

For evaluating $\delta\varphi_i/\delta\rho$, in turn, for the “binding element” one generally uses the Kohn–Sham one-electron potential v_s (10) [77, 88]:

$$\frac{\delta\varphi_i(\mathbf{r}')}{\delta\rho(\mathbf{r})} = \int \frac{\delta\varphi_i(\mathbf{r}')}{\delta v_s(\mathbf{r}'')} \frac{\delta v_s(\mathbf{r}'')}{\delta\rho(\mathbf{r})} d\mathbf{r}''.$$
 (52)

In (52), the functional derivative $\delta\varphi_i/\delta v_s$ can be evaluated in terms of perturbation theory starting from Eq. (9) (i.e., considering δv_s as a small perturbation of the v_s potential, and $\delta\varphi_i$, as the corresponding first order correction to the φ_i one-electron function):

$$\delta\varphi_i(\mathbf{r}) = -\sum_{j \neq i} \frac{\int \varphi_j(\mathbf{r}') \delta v_s(\mathbf{r}') \varphi_i(\mathbf{r}') d\mathbf{r}'}{\varepsilon_j - \varepsilon_i} \varphi_j(\mathbf{r}) = \int \delta v_s(\mathbf{r}') \left[-\sum_{j \neq i} \frac{\int \varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} \varphi_i(\mathbf{r}') \right] d\mathbf{r}'. \quad (53)$$

By the definition of the functional derivative (40), (41),

$$\frac{\delta\varphi_i(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -\sum_{j \neq i} \frac{\varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} \varphi_i(\mathbf{r}') \equiv -G_i(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}'), \quad (54)$$

where G_i is the static one-electron Green function corresponding to the orbital with the index i .

To find the last component $\delta v_s/\delta\rho$ required, one uses the *static linear response function*,

$$\chi(\mathbf{r}, \mathbf{r}') \equiv \frac{\delta\rho(\mathbf{r})}{\delta v_s(\mathbf{r}')} = -2 \sum_i^{\text{occ}} \varphi_i(\mathbf{r}) G_i(\mathbf{r}, \mathbf{r}') \varphi_i(\mathbf{r}'). \quad (55)$$

The physical sense of the χ function is reflected in its name because it describes the reaction of the electron density of the system (in first order perturbation theory) to a minor change in the external potential*. Accordingly, the desired functional derivative $\delta v_s/\delta\rho$ can be formally recorded as an *inverted* linear response function

$$\frac{\delta v_s(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \chi^{-1}(\mathbf{r}, \mathbf{r}'). \quad (56)$$

Equation (56) implies that the following relation is satisfied:

$$\int \chi(\mathbf{r}, \mathbf{r}'') \chi^{-1}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \int \chi^{-1}(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \delta(\mathbf{r} - \mathbf{r}'). \quad (57)$$

Inversion of the linear response function is a technically complex problem, which can be solved by performing expansion in a finite auxiliary basis (which differs from the basis of atomic orbitals) [89], but is numerically unstable in calculations for molecules. Moreover, construction of the linear response function itself (55), which, in turn, requires the construction of the Green function G_i (see Eq. (54)), is a rather expensive procedure, especially because all of the above operations should be performed at each iteration of the self-consistency process. Recall that the initial problem was to construct the local and multiplicative potential v_{xc}^{orb} (51) to substitute the latter into (9) and (10). The whole procedure can only be fulfilled numerically (v_{xc}^{orb} cannot be obtained in analytical form). In practice, however, v_{xc}^{orb} is constructed by an alternative technique (which also implies only numerical solution) called the *optimized effective potential* (OEP) method and discussed below.

OPTIMIZED EFFECTIVE POTENTIAL METHOD (OEP)

In the OEP method [90, 91], the variational problem is formulated differently; instead of seeking the stationary points of the *total* electron energy with respect to variation of density ($\delta E/\delta\rho = 0$), the Kohn–Sham potential (10) is varied for the same purpose; that is, the problem is reduced to seeking an “optimized effective potential” v_s^{OEP} such that

*Equation (55) can readily be obtained from (54) if density equation (3) is taken into account.

$$\frac{\delta E}{\delta v_s^{\text{OEP}}} = 0. \quad (58)$$

These variational problems are equivalent because theoretically they lead to identical results: as shown recently [92], in the framework of DFT for the “basic variable” one can use not only electron density, but also other objects, in particular, the Kohn–Sham potential (10). The functional derivative $\delta E/\delta v_s$ can be conveniently represented as

$$\frac{\delta E}{\delta v_s^{\text{OEP}}} = \sum_i^{\text{occ}} \int \frac{\delta E}{\delta \varphi_i(\mathbf{r}')} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_s^{\text{OEP}}(\mathbf{r})} d\mathbf{r}', \quad (59)$$

where $\delta \varphi_i / \delta v_s^{\text{OEP}}$ is determined in terms of (51); taking into account (2), (9), and (10), $\delta E/\delta \varphi_i$ can be recorded as

$$\frac{\delta E}{\delta \varphi_i(\mathbf{r})} = \left[-\nabla^2 - 2 \sum_K \frac{Z_K}{|\mathbf{r} - \mathbf{R}_K|} + 2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \varphi_i(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{orb}}}{\delta \varphi_i(\mathbf{r})} = 2[\varepsilon_i - v_{\text{xc}}^{\text{orb}}(\mathbf{r})] \varphi_i(\mathbf{r}) + \frac{\delta E_{\text{xc}}^{\text{orb}}}{\delta \varphi_i(\mathbf{r})}, \quad (60)$$

where $v_{\text{xc}}^{\text{orb}}$ is the desired local and multiplicative exchange correlation functional. Substituting (60) and (54) into (58), (59) and taking into account (55) and the fact that the Green function G_i (by construction) is a linear combination of orbitals orthogonal to φ_i , we obtain (after identical transformations) an *integral equation of the OEP method*,

$$\int \chi(\mathbf{r}', \mathbf{r}) v_{\text{xc}}^{\text{orb}}(\mathbf{r}') d\mathbf{r}' = - \sum_i^{\text{occ}} \varphi_i(\mathbf{r}) \int \frac{\delta E_{\text{xc}}^{\text{orb}}}{\delta \varphi_i(\mathbf{r}')} G_i(\mathbf{r}' - \mathbf{r}) d\mathbf{r}'. \quad (61)$$

In the case of pure density functionals, by virtue of (44), Eq. (61) becomes an identity.

The numerical method for solving (61) is not efficient and not stable from computational viewpoint; it is suitable only for calculations of atoms [91]. Moreover, from practical viewpoint, the equation itself has no advantages over the explicit equation for $v_{\text{xc}}^{\text{orb}}$ (51). Nevertheless, the nature of integral equation (61) admits the introduction of quite effective approximations, leading to a considerable simplification of the construction procedure of the $v_{\text{xc}}^{\text{orb}}$ potential. We will discuss in detail one of the approximations actively used in our studies, namely, the *common energy denominator approximation* (CEDA) [93] (which is ideologically fully equivalent to the “*localized Hartree–Fock method*” (LHF)* [94]). The CEDA formalism is also very convenient for discussing a rather popular but rougher approximation used previously, namely the Krieger–Li–Iafrat (KLI) approximation [95].

The major idea of the CEDA [93] is approximation for the one-electron Green function, according to which the differences between the orbital energies corresponding to the “occupied–vacant” orbital pairs in the denominator are replaced with a certain common “mean” value:

$$G_i(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} \approx \sum_{j \neq i}^{\text{occ}} \frac{\varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}')}{\varepsilon_j - \varepsilon_i} + \frac{1}{\Delta \varepsilon} \sum_j^{\text{vac}} \varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}'). \quad (62)$$

The next step is extension of the common energy denominator approximation to the “occupied–occupied” orbital pairs; it leads to the KLI approximation [95], in which due to the completeness of the space of the (orthonormalized) molecular orbitals, the Green function

$$\sum_i |\varphi_i\rangle \langle \varphi_i| = 1, \quad (63a)$$

or

$$\sum_i \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (63b)$$

*This name is not quite suitable because this procedure is applicable to any orbital-dependent functionals, and not only to exact (Hartree–Fock) exchange.

becomes very simple,

$$G_i(\mathbf{r}, \mathbf{r}') \simeq \frac{1}{\Delta\varepsilon} \sum_{j \neq i} \varphi_j(\mathbf{r}) \varphi_j(\mathbf{r}') = \frac{1}{\Delta\varepsilon} [\delta(\mathbf{r} - \mathbf{r}') - \varphi_i(\mathbf{r}) \varphi_i(\mathbf{r}')]. \quad (64)$$

Without detailing the working equations of the KLI approximation, we note that while being simple and attractive from the viewpoint of computational resources, this is a rather rough approach (essentially admitting “averaging” of values with opposite signs!). It has the same disadvantage as the method of direct subtraction of self-interaction [43], namely, it is not invariant under the unitary transformations of the occupied one-electron orbitals.

Let us now return to the CEDA–LHF formalism. We omit the cumbersome intermediate constructions and transformations and give only the final working equations. The desired local and multiplicative exchange correlation potential is constructed as the sum of two terms [94, 93]:

$$v_{xc}(\mathbf{r}) = v_{xc}^{av}(\mathbf{r}) + v_{xc}^{corr}(\mathbf{r}), \quad (65)$$

where v_{xc}^{av} is the orbital-averaged FDO (46) or (48),

$$v_{xc}^{av}(\mathbf{r}) = \frac{\sum_i^{\text{occ}} \varphi_i(\mathbf{r}) [\hat{v}_{xc}^{\text{orb}} \varphi_i](\mathbf{r})}{\rho(\mathbf{r})}, \quad \hat{v}_{xc}^{\text{orb}} = \hat{v}_{xc}^{\rho, \tau}, \quad \hat{v}_{xc}^{\text{hybr}}, \quad (66)$$

and v_{xc}^{corr} is the correction potential also called the “response potential” [96],

$$v_{xc}^{corr}(\mathbf{r}) = \frac{\sum_{i, j}^{\text{occ}} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \langle \varphi_j | v_{xc} - \hat{v}_{xc}^{\text{orb}} | \varphi_i \rangle}{\rho(\mathbf{r})} \quad (67)$$

(the prime at the summation symbol implies that in the sum of (67) we omitted the diagonal term that corresponds to the highest occupied molecular orbital; i.e., $i = j = N^{\text{occ}}$). The average potential v_{xc}^{av} is calculated from (66) directly, while the correction term v_{xc}^{corr} is calculated by using iterations, which generally quickly converge [94]. Note that the structure of the solution in the KLI approximation is similar to that of (65)–(67); the only difference is that in correction potential (67) we neglect all of the “off-diagonal” terms (i.e., the terms corresponding to the condition $i \neq j$).

In the case of 100% exact exchange and neglect of dynamic correlation ($\hat{v}_{xc}^{\text{orb}} = \hat{v}_{xc}^{\text{exact}}$ (49)) the average potential (66) has a special name: Slater potential v_x^S [97]. It can readily be seen that the latter is related by a simple equation to the exact exchange energy density (22):

$$\varepsilon_x^{\text{exact}}(\mathbf{r}) = \frac{1}{2} \rho(\mathbf{r}) v_x^S(\mathbf{r}). \quad (68)$$

Recently, the direct optimization method has become popular. This method uses the OEP representation in the form of the sum of a certain fixed potential and a correction, which can be expanded in an auxiliary basis that is generally different from the atomic orbital basis [98]. However, today the sensitivity of this method to the quality of an auxiliary basis, in particular, to its completeness, is not completely studied (see, e.g., recent publications [99, 100]).

Using the OEP method was described in the literature for transforming the nonlocal exact exchange operator (49) per *se** into the local and multiplicative potential as applied to finite systems in both the KLI [48, 78, 101–104] and CEDA–LHF [15, 94, 105] approximations. For transforming the exact exchange operator *within the nonlocal hybrid potential* (48), using the OEP method was described in the form of the CEDA–LHF approximation [106–111] and in the form of a decomposition into the basis functions [112, 113].

*In cases when 100% exact exchange (19) is used as exchange energy.

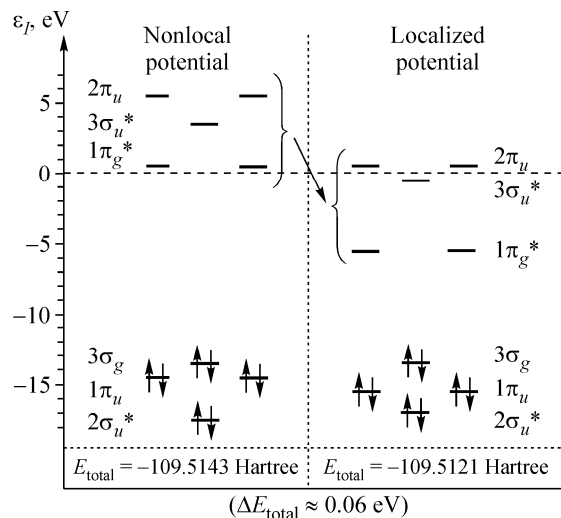


Fig. 2. Localization effect of the authentically nonlocal hybrid potential (operator) for the nitrogen molecule: the total energy of the molecule and the *occupied* one-electron orbital energies vary insignificantly, while the *virtual* orbital energies decrease substantially. Self-consistent calculation with the B88-EXX-LYP hybrid functional ($\alpha_0 = 0.5$, this is often called the “Becke-Half-and-Half-LYP” or, in abbreviated form, “BHandHLYP” in the literature) in the IGLO-IV basis.

Let us consider details of the localization effect of the nonlocal hybrid operator, taking the nitrogen molecule as an illustration. As can be seen in Fig. 2, the difference in the nature of the potentials (operators) is almost insignificant to the total energy of the molecule and to the energies of the *occupied* one-electron orbitals. At the same time, the *virtual* orbital energies decrease considerably, which results in the appearance of greater numbers of “bound” one-electron states (description of the virtual subspace is much more adequate in the case of localized potentials; see [94] for detailed discussion). This effect is very important for calculating the “response” properties in second order perturbation theory (for example, nuclear chemical screening constants) since the *one-electron energy differences* (and the matrix elements between the occupied and virtual orbitals) change significantly.

The construction of the local and multiplicative τ -dependent potential was first described in our work [114], which reported the transformation of FDO (46) by the OEP method (CEDA-LHF approximation). Later we succeeded in obtaining the Kohn–Sham potentials for the more general case of orbital-dependent functionals (see the next section).

To summarize, the Zhao–Morrison–Parr (ZMP) approach [115] is an alternative to the OEP method for the construction of the local and multiplicative potentials. According to this approach, the Kohn–Sham potential can be constructed during iterations, starting from *any* electron density specified as an expansion into the functions of a certain basis. In this case, the origin of density is unimportant because it can be obtained in both self-consistent calculation with a nonlocal hybrid potential and beyond the DFT or Hartree–Fock method, that is, for example, using any highly correlated post-Hartree–Fock method [7] (of the many-particle perturbation theory, multiconfiguration method of self-consistent field, configuration interaction, coupled cluster method, etc.). The ZMP technique was used [108, 116–118] exactly for constructing the Kohn–Sham potentials from the densities obtained in a self-consistent calculation with nonlocal hybrid potentials. While the ZMP method is universal, it is rather labor-consuming and is hardly applicable to large systems; moreover, its numerical stability and the reliability of results obtained with it are dubious. The same properties (chemical screening constants) obtained with the local and multiplicative potentials obtained from the same hybrid FDO (48) in different ways (within the framework of

the OEP method (CEDA–LHF approximation) in one case and using the ZMP procedure in the other) differ widely (see the discussion in [108, 109]). The sources of these differences deserve thorough analysis; nevertheless, it seems more natural to use the OEP method as applied to FDP with the orbital-dependent functionals.

LOCALIZED LOCAL HYBRID (LLH) POTENTIALS

This section discusses the construction of the local and multiplicative potentials for the case of orbital-dependent functionals of more general form, namely, local hybrid functionals (27). As for global hybrids (25), (26), at first we are to obtain the corresponding FDOs $\delta E_{xc}^{\text{loc-hybr}} / \delta \varphi_i$; then the latter are “localized” by the OEP procedure described in the previous section. In contrast to the global hybrids, however, the expression for $\delta E_{xc}^{\text{loc-hybr}} / \delta \varphi_i$ is rather complex and includes much more contributions than $\delta E_{xc}^{\text{hybr}} / \delta \varphi_i$ (48). These expressions were first obtained in our works [119, 120] for several particular cases of the g LMF. Here we give the functional derivative $\delta E_{xc}^{\text{loc-hybr}} / \delta \varphi_i$ in a more general form; we include in the LMF the dependence on all density and orbital ingredients actually used today*:

$$g = g[\rho, |\nabla\rho|, \nabla^2\rho, \tau\{\|\nabla\varphi_i\|_i^{\text{occ}}\}], \quad (69)$$

and consider that the $\varepsilon_x^{\text{DFT}}$ (semi)local component depends only on the density or its gradient (i.e., belongs to the LDA or GGA, but not meta-GGA** type). Thus,

$$\begin{aligned} \frac{\delta E_{xc}^{\text{loc-hybr}}}{\delta \varphi_i} &\equiv 2\hat{v}_{xc}^{\text{loc-hybr}} \varphi_i = (g\hat{v}_{xc}^{\text{exact}} \varphi_i + \hat{v}_{xc}^{\text{exact}} \{g\varphi_i\}) + 2 \left[(1-g)v_x^{\text{DFT}} + v_c^{\text{DFT}} + (\nabla g) \cdot \left(\frac{\partial \varepsilon_x^{\text{DFT}}}{\partial \nabla \rho} \right) \right] \varphi_i + \\ &\frac{\partial g}{\partial \varphi_i} (\varepsilon_x^{\text{exact}} - \varepsilon_x^{\text{DFT}}) - \nabla \left[\frac{\partial g}{\partial \nabla \varphi_i} (\varepsilon_x^{\text{exact}} - \varepsilon_x^{\text{DFT}}) \right] + \frac{1}{2} \nabla^2 \left[\frac{\partial g}{\partial \nabla^2 \varphi_i} (\varepsilon_x^{\text{exact}} - \varepsilon_x^{\text{GGA}}) \right], \end{aligned} \quad (70)$$

where

$$v_x^{\text{DFT}} = \frac{\partial \varepsilon_x^{\text{DFT}}}{\partial \rho} - \nabla \left(\frac{\partial \varepsilon_x^{\text{DFT}}}{\partial \nabla \rho} \right), \quad (71)$$

and the \hat{v}_x^{exact} operator is determined by (49). In this case, we do not impose any limitations on E_c^{DFT} ; in particular, one can use any orbital-dependent correlation functional with substitution (47), which is quite justifiable here. It can readily be seen that in the limiting case of the constant LMF ($g = \text{const} = a_0$), all contributions in (70) that contain the derivatives of LMF are zero; thus, (70) is reduced to (48). Transforming the last line of (70) and the $(\nabla g) \cdot \left(\frac{\partial \varepsilon_x^{\text{DFT}}}{\partial \nabla \rho} \right)$ contribution, we ultimately

obtain

$$\begin{aligned} \frac{\delta E_{xc}^{\text{loc-hybr}}}{\delta \varphi_i} &\equiv 2\hat{v}_{xc}^{\text{loc-hybr}} \varphi_i = (g\hat{v}_{xc}^{\text{NL}} \varphi_i + \hat{v}_{xc}^{\text{NL}} \{g\varphi_i\}) + 2 \left[(1-g)v_x^{\text{DFT}} + v_c^{\text{DFT}} \right] \varphi_i + 2 \frac{\partial \varepsilon_x^{\text{GGA}}}{\partial |\nabla \rho|} \left\{ \frac{\partial g}{\partial \rho} |\nabla \rho| + \right. \\ &\left. \frac{\partial g}{\partial |\nabla \rho|} \frac{(\nabla \rho) \cdot (\nabla |\nabla \rho|)}{|\nabla \rho|} + \frac{\partial g}{\partial \nabla^2 \rho} \frac{(\nabla \rho) \cdot [\nabla(\nabla^2 \rho)]}{|\nabla \rho|} + \frac{\partial g}{\partial \tau} \frac{(\nabla \rho) \cdot (\nabla \tau)}{|\nabla \rho|} \right\} \varphi_i + 2 \left[\frac{\partial g}{\partial \rho} (\varepsilon_x^{\text{exact}} - \varepsilon_x^{\text{DFT}}) - \right. \end{aligned}$$

*The spatial derivatives of density and the third and higher order orbitals are not used.

**According to our recent studies, the space-dependent mixing of exact exchange with semilocal exchange of higher order (meta-GGA) is of formal interest only.

$$\nabla \left[\frac{\partial g}{\partial |\nabla \rho|} \frac{(\nabla \rho)}{|\nabla \rho|} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \right] + \nabla^2 \left(\frac{\partial g}{\partial \nabla^2 \rho} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \right) \Big] \varphi_i - \left[\nabla \left(\frac{\partial g}{\partial \tau} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \right) \right] (\nabla \varphi_i) - \frac{\partial g}{\partial \tau} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \nabla^2 \varphi_i. \quad (72)$$

While being apparently cumbersome, Eq. (72) contains the derivatives $\partial g/\partial \rho$, $\partial g/\partial |\nabla \rho|$, $\partial g/\partial \nabla^2 \rho$, and $\partial g/\partial \tau$, which are readily calculated (from a particular analytical form of LMF, e.g., (29), (32), or (34)), as well as the "natural" ingredients generated in any quantum-chemical program that includes DFT (in particular, $|\nabla \rho|$, $\nabla^2 \rho$, and the scalar derivatives $(\nabla \rho) \cdot (\nabla |\nabla \rho|)$, $(\nabla \rho) \cdot (\nabla \tau)$). Several contributions, however, deserve more detailed discussion. It should be emphasized that in quantum-chemical programs (except the numerical quantum-chemical programs such as NUMOL [121]), the Kohn–Sham potential (10) is always used in the form of matrix elements calculated in an atomic orbital (AO) basis. Therefore, it is not necessary to differentiate complex expressions (e.g., to explicitly calculate the contributions $\nabla \left(\frac{\partial g}{\partial |\nabla \rho|} \frac{(\nabla \rho)}{|\nabla \rho|} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \right)$ or $\nabla^2 \left(\frac{\partial g}{\partial \nabla^2 \rho} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) \right)$ on the right side of (72)). Instead, one can perform transformations (using "three-dimensional integration by parts") of the following type:

$$\langle \chi_\mu | (\nabla F) \chi_\nu \rangle \equiv \int \chi_\mu(\mathbf{r}) (\nabla F(\mathbf{r})) \chi_\nu(\mathbf{r}) d\mathbf{r} = - \int F(\mathbf{r}) [\nabla (\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}))] d\mathbf{r}, \quad (73)$$

taking into account that all functions that can be integrated in (73) are finite (vanish at infinity)*. Transformation (73) may be used in sequence as long as necessary in order to avoid undesirable differentiation of complex equations containing, e.g., the exact exchange energy density (or calculations of third order derivatives with respect to density in $\frac{\partial g}{\partial \nabla^2 \rho} (\nabla \rho) \cdot [\nabla (\nabla^2 \rho)] / |\nabla \rho|$, etc.). As a result, differentiation (no more than double differentiation) is used only for the $\{\chi_\mu\}$ basis AOs, which is quite a routine problem. To summarize, we give the final equation for the matrix element of FDO corresponding to the local hybrid functional (27),

$$\langle \chi_\mu | \hat{v}_{xc}^{\text{loc-hybr}} | \chi_\nu \rangle = \langle \chi_\mu | \hat{A} + B | \chi_\nu \rangle + \langle \nabla \chi_\mu | C | \chi_\nu \rangle + \langle \chi_\mu | C | \nabla \chi_\nu \rangle + \langle \nabla \chi_\mu | D | \nabla \chi_\nu \rangle + \langle \nabla^2 \chi_\mu | E | \chi_\nu \rangle + \langle \chi_\mu | E | \nabla^2 \chi_\nu \rangle, \quad (74)$$

where

$$\hat{A} = (g \hat{v}_x^{\text{NL}} + \hat{v}_x^{\text{NL}} g) / 2 \quad (75)$$

is the nonlocal operator, while all other operators are local:

$$B = (1-g) v_x^{\text{DFT}} + v_c^{\text{DFT}} + \frac{\partial g}{\partial \rho} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) + g \left(v_x^{\text{DFT}} - \frac{\partial \epsilon_x^{\text{DFT}}}{\partial \rho} \right), \quad (76)$$

$$C = \left(\frac{\partial g}{\partial |\nabla \rho|} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}) - g \frac{\partial \epsilon_x^{\text{DFT}}}{\partial |\nabla \rho|} \right) \frac{\nabla \rho}{|\nabla \rho|}, \quad (77)$$

$$D = \left(2 \frac{\partial g}{\partial \nabla^2 \rho} + \frac{1}{2} \frac{\partial g}{\partial \tau} \right) (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}), \quad (78)$$

$$E = \frac{\partial g}{\partial \nabla^2 \rho} (\epsilon_x^{\text{exact}} - \epsilon_x^{\text{DFT}}). \quad (79)$$

*Using transformation (73) one can easily show that the expressions for the kinetic energy density

$\frac{1}{2} \sum_{i_\sigma=1}^{N_{\sigma,\text{occ}}} |\nabla \varphi_{i_\sigma}(\mathbf{r})|^2$ and $-\frac{1}{2} \sum_{i_\sigma=1}^{N_{\sigma,\text{occ}}} \varphi_{i_\sigma}^*(\mathbf{r}) \nabla^2 \varphi_{i_\sigma}(\mathbf{r})$ are equivalent and one can illustrate the problem of ambiguous determination of the exchange energy density (see above).

To summarize, it is worthwhile to refer to the method for calculating the exact exchange energy density $\varepsilon_x^{\text{exact}}$. Evidently, explicit calculation of $\varepsilon_x^{\text{exact}}$ (directly using its definition (22)) at each point of the numerical integration net is an extremely labor-consuming problem. Instead of this procedure, the authors of [94] used completeness (resolution of identity) (63), which (in the nonorthogonal basis) is as follows:

$$\delta(\mathbf{r} - \mathbf{r}') = \sum_{\mu} \sum_{\nu} \chi_{\mu}(\mathbf{r})(\mathcal{S}^{-1})_{\mu\nu} \chi_{\nu}(\mathbf{r}'), \quad (80)$$

where \mathcal{S}^{-1} is the inverse of the matrix of the overlap integrals of basis functions. Using the expansion of the molecular orbitals

$$\varphi_i = \sum_{\mu} C_{\mu i} \chi_{\mu} \quad (81)$$

and Eq. (80), one can record the exact exchange energy as

$$\begin{aligned} \varepsilon_x^{\text{exact}}(\mathbf{r}) &= -\frac{1}{2} \sum_{i,j}^{\text{occ}} \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \int \frac{\varphi_i(\mathbf{r}') \varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' = \frac{1}{2} \sum_i^{\text{occ}} \varphi_i(\mathbf{r}) [\hat{V}_x^{\text{exact}} \varphi_i](\mathbf{r}) = \frac{1}{2} \sum_i^{\text{occ}} \varphi_i(\mathbf{r}) \int \delta(\mathbf{r} - \mathbf{r}') [\hat{V}_x^{\text{exact}} \varphi_i](\mathbf{r}') d\mathbf{r}' = \\ &= \frac{1}{2} \sum_{\mu} \sum_{\nu} \chi_{\mu}(\mathbf{r})(\mathcal{S}^{-1})_{\mu\nu} \sum_{\kappa} \chi_{\kappa}(\mathbf{r}) \sum_{\lambda} \left(\sum_i^{\text{occ}} C_{\lambda i} C_{\kappa i} \right) \int \chi_{\nu}(\mathbf{r}') [\hat{V}_x^{\text{exact}} \chi_{\lambda}](\mathbf{r}') d\mathbf{r}' = \\ &= \frac{1}{2} \sum_{\mu} \sum_{\nu} \sum_{\lambda} \sum_{\kappa} (\mathcal{S}^{-1})_{\mu\nu} K_{\nu\lambda} P_{\lambda\kappa} X_{\kappa\mu}(\mathbf{r}) = \frac{1}{2} \text{Tr}[\mathcal{S}^{-1} \mathbf{K} \mathbf{P} \mathbf{X}(\mathbf{r})], \end{aligned} \quad (82)$$

where

$$X_{\kappa\mu} = \chi_{\kappa}(\mathbf{r}) \chi_{\mu}(\mathbf{r}); \quad (83)$$

$$P_{\lambda\kappa} = \sum_i^{\text{occ}} C_{\lambda i} C_{\kappa i} \quad (84)$$

are the density matrix elements; and

$$K_{\nu\lambda} = \int \chi_{\nu}(\mathbf{r}') [\hat{V}_x^{\text{exact}} \chi_{\lambda}](\mathbf{r}') d\mathbf{r}' \quad (85)$$

are the exact exchange matrix elements, which are readily accessible in any standard quantum-chemical program (except “pure functional-density” programs such as deMon2K [122]). We also used the resolution of identity *twice* in calculating the integrals of the nonlocal operator \hat{A} (75). It should be emphasized that expansion (80) is performed in a *finite* basis and hence is an additional approximation. For minimizing the error introduced by representation (82) this is required if contracted AO basis sets are used (the AO bases should be of high quality). Details of this technique are given in our publication [119]*.

The local and multiplicative potentials obtained by using the OEP method (in the CEDA/LHF approximation) for FDO (72), (74) are called the localized local hybrid (LLH) potentials. To avoid misunderstanding, the local and multiplicative potentials constructed from FDO (48) of the global hybrids are called here the localized *global* hybrid (LGH) potentials.

RESULTS AND DISCUSSION

All the necessary algorithms and equations described above were implemented with our MAG-ReSpect software [123], with which we fulfilled all calculations. To calculate the thermochemical properties we used the cc-pVQZ basis sets [124, 125] (without the *g* functions). The basis sets from the IGLO family were used to calculate the magnetic resonance parameters [126]. In calculations of the chemical screening constants, the calibrating (gradient) invariance problem was solved within the framework of the GIAO [127] (LGH potentials) and IGLO [126] (LLH potentials) approaches. In *g* tensor calculations for transition metal complexes, the common gauge origin was chosen to be on the metal atom. The magnetic resonance parameters considered in this work were calculated in second order perturbation theory using the procedures described in [83-85, 128].

*Specially selected auxiliary bases may be an alternative to the decontracted AO bases.

Thermochemical calculations with the local hybrid functionals. Let us consider the atomization energies of molecules from the standard G2-1 (55 molecules and radicals) [62, 63] and G2 (148 molecules) test sets [129]*. All total energies were taken from the non-self-consistent calculations with the orbitals obtained in the local density approximation (post-LDA calculations, see above). Table 1 lists the data of the simplest statistical analysis (mean *absolute* deviations and mean deviations (including the sign) of the calculated values from experiment) for atomization energies obtained with the local hybrid functionals using the LMFs of two types, namely, the functions that depend on the t parameter (29) (t -LMF) and those that depend on the dimensionless electron density gradient s (33) (s -LMF). We used the experimental data of [130]. For comparison, Table 1 also lists the results obtained with the global hybrid functionals, both one-parameter (25) and B3LYP (26) functionals. As mentioned above, the atomization energies are seriously underestimated by the local hybrid functionals (27) with the initially suggested [61] unscaled t -LMF (29). In this case, however, the result depends significantly on the type of the admixed “density functional” exchange (ϵ_x^{DFT}); with the GGA (B88 and PBE) functionals, the errors are much smaller than those with the local exchange (S). The difference between the correlation functionals used (LYP, PKZB, VWN) seems to be much less significant. The scaling of t -LMF, that is, a transition from (29) to (32) improves the results by an order of magnitude, which is especially pronounced for the Lh -SVWN scheme (for notation used, see note a to Table 1). It is interesting to note that with LMF (32) the best results were obtained when *local* exchange was mixed with exact exchange; substitution by GGA type exchange (B88) did not afford an equally low mean absolute deviation *for any* value of $0 \leq \lambda \leq 1$ (see (32); the corresponding data are not given in Table 1). An important peculiarity of the Lh -SVWN scheme is its very high stability against expansion of the test set of molecules by a factor of ~ 3 , that is, in passing from G2-1 to G2 (full set); the mean absolute deviation (3.6 kcal/mol) (minimized with respect to the λ parameter on molecules from the G2-1 set) increased by only 0.2 kcal/mol. Using the Lh -SLYP scheme, one can reach even a smaller absolute error within the “small” G2-1 set (2.9 kcal/mol), but it increases by a factor of more than 1.5 on passing to the G2 set.

Comparable results (of the same quality) can also be obtained with s -LMF (34); in this case, however, using the GGA correlation of LYP is obviously preferable. Table 1 also includes the data obtained with the LMF erf (0.24 s).

A comparison of the data obtained with the local hybrid scheme with the results of calculations with the *one-parameter* global hybrids shows that the *local* hybrids are obviously advantageous. The results of comparable quality can

TABLE 1. Statistical Analysis of the Atomization Energies of Molecules (kcal/mol) Obtained with Different Exchange Correlation Functionals

Functional				Small test set G2-1 ⁱ (55 molecules)			Complete test set G2 ^j (148 molecules)		
Type	Detailed description			Mean abs. deviation	Mean deviation	Max. deviation	Mean abs. deviation	Mean deviation	Max. deviation
	Exchange ^a	LMF ^b or a_0 ^c	Corre- lation ^d						
1	2	3	4	5	6	7	8	9	10
Global hybrids	B3LYP ($a_0 = 0.2$) (see Eq. (26))			2.7	-0.9	-15.3 (SO ₂)	4.1	-3.2	-24.8 (SiCl ₄)
	S ^e	0.47	VWN	10.3	5.7	39.5 (C ₂ H ₆)	22.1	18.6	71.1 (C ₄ H ₁₀) ^f
	S ^e	0.54	LYP	7.0	2.0	27.5 (C ₂ H ₆)	18.7	15.3	63.5 (C ₆ H ₆)
	B88 ^e	0.13	LYP	2.9	-1.4	-11.3 (SO ₂)	6.9	-5.8	-29.4 (SiCl ₄)

*See the notes to Table 1.

TABLE 1. (Continued)

1	2	3	4	5	6	7	8	9	10
Local hybrids	B88 ^g	t	LYP	19.6 ^h	—	-59.3 ^h	—	—	—
	PBE ^g	t	PKZB	13.0 ^h	—	-51.7 ^h	—	—	—
	S ^g	t	VWN	38.2	-37.9	-102.5	—	—	—
		$0.48t$	VWN	3.6	0.2	-13.2 (N ₂)	3.8	0.5	-16.6 (CN) ₂
	S ^f	$0.50t$	LYP	2.9	-0.6	-8.1 (N ₂)	4.9	3.3	29.3 (C ₂ F ₄)
		$\left(\frac{s}{0.73+s}\right)^2$	LYP	2.6	-0.73	-11.1 (N ₂)	4.5	2.7	20.8 (C ₂ F ₄)
		$\left(\frac{s}{0.84+s}\right)^2$	VWN	5.1	1.0	-14.3 (N ₂)	5.9	2.0	-19.8 (CN) ₂
$\text{erf}(0.24s)$		LYP	2.9	-0.6	-10.6 (N ₂)	3.9	1.9	21.8 (C ₂ F ₄)	

^aThese are mixed with the exact exchange E_x^{DFT} or ϵ_x^{DFT} in (25)-(27). Other symbols used in the literature for the global hybrids are S-EXX-VWN, S-EXX-LYP, and B88-EXX-LYP, respectively (where “EXX” (“EXact eXchange”) indicates that an exact exchange admixture is present) with an explicit indication to the value of the exact exchange admixture a_0 . For the local hybrids, we use the notation *Lh*-BLYP, *Lh*-PBEPKZB, *Lh*-SVWN, and *Lh*-SLYP, respectively, with an explicit indication to the local mixing function.

^bFor local hybrids (Eq. (27)).

^cFor global hybrids (Eqs. (25) and (26)).

^d E_c^{DFT} in (25)-(27).

^e*One-parameter* functionals: the numerical values of the parameters in the LMF (or a_0) minimize the mean absolute deviations of the atomization energies from the experimental values for molecules from the G2-1 set.

^f*n*-Butane (*trans*-conformation).

^gTest functionals without varied parameters.

^hThe data of [61] correspond to the non-self-consistent *post-Hartree-Fock* calculations (in contrast to all other data given in the table, which were obtained with the orbitals from the self-consistent calculation in the *local density approximation* (post-LDA)).

ⁱThe G2-1 set: CN, CO, CO₂, F₂, Li₂, LiF, N₂, NO, O₂, Cl₂, Na₂, NaCl, P₂, S₂, Si₂, BeH, C₂H₂, C₂H₄, C₂H₆, CH, CH₂ (¹A₁), CH₂ (³B₁), CH₃, CH₄, H₂CO, H₂O, H₂O₂, CH₃OH, HCN, HCO, HF, LiH, N₂H₄, NH, NH₂, NH₃, H₂S, OH, HCl, PH₂, PH₃, Si₂H₆, SiH₂ (¹A₁), SiH₂ (³B₁), SiH₃, SiH₄, CH₃Cl, ClF, ClO, CS, CH₃SH, HOCl, SiO, SO, and SO₂.

^jIn addition to 55 molecules from G2-1, the G2 set includes BF₃, AlF₃, BCl₃, AlCl₃, CF₄, CCl₄, COS, CS₂, CF₂O, SiF₄, SiCl₄, N₂O, ClNO, NF₃, PF₃, O₃, F₂O, ClF₃, (CN)₂, H₂, HS, CCH, NO₂, and a number of organic molecules with up to six carbon atoms.

only be obtained with the B3LYP functional, containing two purely fitting parameters (a_c and a_x) in addition to the exact exchange admixture a_0 , which are dubious from the viewpoint of their physical sense (see (26)).

To summarize, one can argue that the local hybrid functionals, in their exchange part, present a sound alternative to the generalized gradient approximation per se. In other words, in the given scheme, the exchange energy densities of two *fundamental* types, namely, of local (14), (15) and exact (22) types, are mixed at each point of space; good thermochemical results can be obtained using *only one* fitting parameter. This is an obvious advantage over modern DFT, generally tending to use too many empirical parameters. Since the dynamic correlation energy is not involved in the local hybrid scheme (see (27)), investigation of its effect on the result is not an independent problem unrelated to the properties of the local mixing functions used. A detailed discussion of the local hybrid functionals of different types as applied to thermochemistry can be found in [64, 66]. It should be mentioned that, according to our preliminary data [65], the *Lh*-SVWN scheme with LMF (32)

also permits us to obtain high accuracy for the barrier heights of reactions, which is a traditionally complex problem for density functional theory (generally, one can obtain acceptable accuracy in calculating *either* the atomization energies *or* the reaction barriers; one of the rare exceptions is given in [131], in which the aim is achieved by introducing a set of additional fitting parameters).

Chemical screening constants obtained with the LGH potentials. Table 2 compares the chemical screening constants obtained in different calculations for 22 small molecules including the elements of the major subgroups. It can readily be seen that the same *global* hybrid functionals B3-PW91 and B88-EXX-PW91 ($a_0 = 0.5$) lead to absolutely different results, which depend on the method of implementing the corresponding potentials (operators). In the former case, these are iterative solutions of coupled equations (see above) with the $\hat{v}_{xc}^{\text{hybr}}$ nonlocal operators, which are the functional derivatives of hybrid functionals with respect to orbitals (Eq. (48)); in the latter case, these are direct (“one-pass”) calculations with the potentials localized by the OEP method in the CEDA/LFH approximation (in Table 2, the locality of these potentials is designated by the letter “L” in parentheses: B3(L)-PW91 and B88-EXX(L)-PW91, respectively). Evidently, simple localization of the hybrid potentials decreases the mean absolute deviation from the experimental data by a factor of two for B3-PW91 and by a factor of 6 (!) for B88-EXX-PW91 ($a_0 = 0.5$). One of the major reasons for this dramatic difference is a more adequate description of the subspace of virtual orbitals, which is especially important for calculations with second order perturbation theory (see above).

TABLE 2. Chemical Screening Constants (ppm) Calculated with the Nonlocal (FDO) and Localized (LGH) Global Hybrid Potentials

Molecule	Nucleus	FDO ^a		LGH				Experiment ^b	
		B3-PW91	B88-EXX-PW91, $a_0 = 0.5$	B3(L)-PW91	B88-EXX(L)-PW91				B88-PW91
					$a_0 = 0.4$	$a_0 = 0.5$	$a_0 = 0.6$		
1	2	3	4	5	6	7	8	9	10
C ₂ H ₂	C	108.1	110.9	109.4	112.4	113.6	114.7	107.4	117.2
C ₂ H ₄	C	47.3	51.5	49.5	54.3	56.3	58.2	45.9	64.5
CH ₃ F	C	106.7	114.9	103.8	107.0	108.1	109.2	101.8	116.8
	F	463.4	473.6	462.9	469.1	472.0	474.8	455.5	456.6
CH ₄	C	188.7	192.1	188.8	191.2	192.3	193.3	186.8	195.1
CHF ₃	C	55.6	67.4	52.1	56.7	58.6	60.4	48.8	68.4
	F	261.2	280.8	258.4	269.5	274.5	279.3	247.4	267.3
CO	C	-18.0	-21.6	-12.0	-8.6	-7.3	-6.0	-14.1	1.0
	O	-82.7	-85.7	-64.2	-49.0	-41.9	-34.8	-79.2	-62.3
CO ₂	C	51.5	52.0	54.8	58.2	59.5	60.8	52.6	58.8
	O	212.4	215.2	218.7	226.3	230.0	233.5	210.9	223.4
F ₂	F	-246.9	-214.6	-258.0	-246.3	-241.6	-237.0	-265.5	-234.2
H ₂ CO	C	-24.1	-18.3	-24.5	-20.5	-19.1	-17.6	-26.5	-4.4±3
H ₂ O	O	327.9	329.3	330.9	334.6	336.5	338.3	326.9	324±1.5
H ₂ S	S	713.3	722.6	719.6	733.0	738.6	744.1	709.0	752.0
HCl	Cl	941.1	950.3	945.2	955.8	960.4	964.8	936.1	952.0
HCN	C	69.9	70.0	72.6	75.1	76.1	77.0	71.1	82.1
	N	-47.8	-48.8	-36.1	-25.9	-21.5	-17.1	-44.6	-20.4
HF	F	411.7	413.9	414.7	418.8	420.8	422.8	410.1	410.1
N ₂	N	-91.7	-100.0	-78.6	-71.3	-68.1	-64.9	-84.8	-61.6±0.5
N ₂ O	N _{term}	83.6	75.7	94.7	100.4	102.8	105.2	90.1	99.5

TABLE 2. (Continued)

1	2	3	4	5	6	7	8	9	10
	N _{central}	-7.0	-15.6	5.3	11.4	13.9	16.3	0.9	11.3
	O	172.5	171.9	183.3	192.9	197.6	202.1	173.1	180.5
NH ₃	N	255.9	257.9	257.7	260.7	262.1	263.5	254.7	264.5
O ₃	O _{central}	-1113	-1540	-862.9	-830.3	-816.4	-802.9	-889.2	-744
	O _{term}	-1691	-2050	-1404	-1330	-1297	-1265	-1470	-1310
P ₂ H ₂	P	-304.7	-314.9	-257.1	-220.1	-205.0	-190.4	-284.6	-166
PH ₃	P	572.9	584.2	574.9	585.5	589.8	594.0	567.4	594
PN	P	-50.3	-69.1	-13.1	9.9	19.8	29.5	-32.4	53
	N	-428.3	-450.0	-383.3	-355.9	-343.3	-330.8	-409.1	-349
SO ₂	S	-256.7	-289.6	-211.4	-190.2	-181.5	-172.8	-226.0	-125.9
	O	-284.6	-289.7	-245.1	-214.2	-199.7	-185.7	-276.3	-225.1
	Mean absolute deviation	50,5	77.5	24.5	15.2	13.9	14.6	34.4	
	Mean deviation	-49.8	-73.8	-23.2	-10.3	-4.6	0.9	-34.2	

^aSelf-consistent calculations by (9) and (10) with the \hat{v}_{xc}^{hybr} nonlocal and nonmultiplicative operator defined in (48).

^bSee [109] for detailed references to the experimental data.

The second conclusion concerning the LGH potentials is considerable difference between the thermochemically optimum value of the a_0 parameter (which equals 0.2 if we take the B3 scheme as a basis, see (26)) and the values of a_0 that lead to the best chemical screening constants (of the order of 0.5-0.6). A difference as large as this can be interpreted as evidence of the “insufficient universality” of the traditional (global) hybrid functionals, which still demand specific fitting for the property being calculated because, in the ideal case, a functional should describe equally well the thermochemical and other properties without any reparametrizations.

For comparison Table 2 also lists the results obtained by using the typical GGA (B88-PW91) potential, which are not quite satisfactory compared with the B88-EXX(L)-PW91 ($a_0 = 0.5$) potential. It should be recognized, however, that within the framework of GGA one can obtain the same level of accuracy for the screening constants as when calculations are performed with the LLH potentials (see, e.g., the KT family of functionals [132, 133]), but this result is achieved by introducing rather artificial derivations and additional fitting parameters.

Electronic g tensors of transition metal complexes obtained with the LGH potentials. Table 3 lists the calculated shifts of the components of the g tensors for nine metal complexes of the first row of transition metals. As in the case of the chemical screening constants, Table 3 compares the results obtained with the same nonlocal and localized hybrid potentials. At first sight, the effect of localization of the potentials is not so pronounced here; moreover, the B3(L)-PW91 potential even leads to worse results compared with the nonlocal B3-PW91 potential. Nevertheless, the increased exact exchange admixture yields better agreement with experiment only in the case of localized potentials. It is interesting to note that the optimum values of a_0 in this case lie in the same range (0.5-0.6) as for screening constants. This coincidence permits us to draw a pragmatic conclusion about the efficiency of hybrid functionals with large exact exchange admixtures for calculating magnetic resonance parameters of “response” type on condition of self-consistent implementation of these functionals in the form of localized potentials. Details of the discussion of the LGH potentials for the g tensors of transition metal complexes and screening constants of the compounds of elements from the major subgroups are found in our publications [109-111].

Chemical screening constants obtained with the LGH potentials [120]. This section demonstrates the possibility of calculating the nonthermochemical properties using the local hybrid functionals for the chemical screening constants of the same 22 compounds of nontransition elements that were used for evaluating the LGH potentials (see above). Table 4

TABLE 3. Shifts of the g Tensor Components for Transition Metal Complexes (thousandths) a Calculated with the Nonlocal (FDO) and Localized (LGH) Global Hybrid Potentials

Compound	g Tensor	FDO ^b		LGH				Experiment ^c	
		B3-PW91	B88-EXX-PW91, $a_0 = 0,5$	B3(L)-PW91	B88-EXX(L)-PW91				
					$a_0 = 0.4$	$a_0 = 0.5$	$a_0 = 0.6$		
Co(CO) ₄	Δg_{\parallel}	5.9	29.9	7.8	12.3	14.6	16.6	4.0	3.6
	Δg_{\perp}	88.8	115.9	87.5	93.5	96.8	100.0	78.9	127.6
CrOF ₄ ⁻	Δg_{\parallel}	-22.7	-33.4	-22.9	-28.5	-31.3	-34.1	-17.0	-43
	Δg_{\perp}	-30.2	-45.7	-31.0	-35.6	-37.8	-39.6	-25.5	-34
CrOCl ₄ ⁻	Δg_{\parallel}	15.8	6.5	11.6	4.2	0.8	-2.2	18.5	-10
	Δg_{\perp}	-25.8	-47.2	-26.6	-31.9	-33.7	-35.0	-19.4	-25
Cu(NO ₃) ₂	Δg_{zz}	157	275	132.8	157.5	172.5	190.4	113.6	263.8
	Δg_{yy}	39.7	71.5	32.1	38.8	42.9	47.7	27.0	49.9
	Δg_{xx}	40.8	71.5	35.4	43.7	48.8	55.1	29.2	49.9
Fe(CO) ₅ ⁺	Δg_{\parallel}	-3.2	-7.5	-1.4	-1.6	-1.7	-1.8	-1.4	-1.5
	Δg_{\perp}	65.9	89.5	53.8	55.8	56.9	57.8	49.6	79.15
Mn(CO) ₅	Δg_{\parallel}	-2.6	-5.5	-1.6	-2.3	-2.8	-3.6	-1.3	-2.3
	Δg_{\perp}	27.4	32.5	23.1	22.8	22.4	21.7	22.4	35.7
MnO ₃	Δg_{\parallel}	2.9	16.5	0.8	-2.8	-4.2	-5.4	3.1	-0.4
	Δg_{\perp}	2.7	90.6	-3.2	-11.7	-16.6	-20.9	2.9	4.7
Ni(CO) ₃ H	Δg_{\parallel}	3.5	13.6	3.9	6.3	7.5	8.8	1.7	1.9
	Δg_{\perp}	64.1	157.4	45.2	49.1	51.2	53.7	41.7	65.1
TiF ₃	Δg_{\parallel}	-1.4	-1.4	-1.4	-1.7	-1.7	-1.7	-1.2	-8.6
	Δg_{\perp}	-48.8	71.4	-48.5	-75.8	-106.2	-169.5	-32.8	-116
Mean absolute deviation		17.0	30.3	21.0	17.2	14.4	15.8	25.0	
Mean deviation		-3.2	24.2	-7.5	-7.8	-8.5	-10.7	-7.7	

^a“Thousandths,” i.e., the values of $\Delta g_{uu} = g_{uu} - g_e$ ($g_e = 2.002319\dots$, $u = x, y, z$) multiplied by 10^3 .

^bSee Note “a” to Table 2.

^cSee [110] for detailed references to the experimental data.

summarizes data for two local hybrid schemes, Lh -SVWN and Lh -SLYP, with two different types of local mixing functions: t -LMF (32) and s -LMF (34), respectively. The results are given for two values of the λ parameter in each case, namely, the thermochemically optimum value (in the sense of minimization of the mean absolute deviation of the atomization energies of molecules from the G2-1 test set, see Table 1) and the optimum value for screening constants. As can be seen from Table 4, the results of calculations with the LMFs of different types are comparable in quality to one another and to the data obtained with the use of the LGH potentials (see Table 2). However, s -LMF (34) is less sensitive to the variation of the λ parameter and provides slightly higher accuracy compared with the scaled t -LMF (32), probably, as a consequence of the regular asymptotic behavior of the corresponding potential (see the discussion above).

Table 4 also lists the mean LMF value for each of the above-discussed potentials. It deserves special discussion because this is some kind of an analog of the a_0 parameter, which describes the global hybrid functionals (potentials) and is defined in the following way:

$$\bar{a}_0 = \int \rho(\mathbf{r})g(\mathbf{r})d\mathbf{r} / \int \rho(\mathbf{r})d\mathbf{r}, \quad (86)$$

TABLE 4. Chemical Screening Constants (ppm) Calculated with the Localized Local Hybrid (LLH) Potentials

Molecule	Nucleus	$Lh(L)$ -S-VWN, LMF = λt		$Lh(L)$ -S-LYP, LMF = $\left(\frac{s}{\lambda + s}\right)^2$		Experiment ^c
		$\lambda = 0.48^a$	$\lambda = 0.80^b$	$\lambda = 0.73^a$	$\lambda = 0.50^b$	
C ₂ H ₂	C	110.6	116.6	111.8	113.8	117.2
C ₂ H ₄	C	51.6	59.3	53.8	56.6	64.5
CH ₃ F	C	104.4	107.1	106.5	107.4	116.8
	F	464.8	462.1	467.0	468.4	456.6
CH ₄	C	190.2	189.2	194.7	194.9	195.1
CHF ₃	C	53.9	59.7	56.0	57.8	68.4
	F	259.5	271.2	255.2	261.2	267.3
CO	C	-6.7	2.1	-2.2	0.3	1.0
	O	-55.0	-34.6	-49.4	-39.7	-62.3
CO ₂	C	57.0	61.9	58.7	60.3	58.8
	O	224.4	233.4	228.7	233.2	223.4
F ₂	F	-264.8	-254.4	-237.5	-232.1	-234.2
H ₂ CO	C	-22.7	-11.4	-21.2	-18.0	-4.4±3
H ₂ O	O	334.9	335.0	338.4	339.2	324±1.5
H ₂ S	S	730.1	727.9	744.5	745.0	752.0
HCl	Cl	958.8	958.5	966.9	968.0	952.0
HCN	C	74.7	80.5	77.3	79.1	82.1
	N	-31.0	-14.9	-29.4	-23.0	-20.4
HF	F	419.0	420.5	420.8	422.1	410.1
N ₂	N	-71.7	-58.9	-66.0	-60.6	-61.6±0.5
N ₂ O	N _{term}	100.4	108.1	104.9	108.1	99.5
	N _{central}	9.0	16.4	11.8	15.0	11.3
	O	189.0	196.0	194.7	199.4	180.5
NH ₃	N	260.7	259.8	265.5	265.8	264.5
O ₃	O _{central}	-849.9	-806.7	-824.2	-804.5	-744
	O _{term}	-1399	-1316	-1337	-1299	-1310
P ₂ H ₂	P	-259.0	-207.9	-255.4	-236.7	-166
PH ₃	P	577.6	573.4	594.1	594.0	594
PN	P	-17.3	14.7	-8.9	4.6	53
	N	-371.5	-339.3	-363.5	-348.0	-349
SO ₂	S	-215.2	-186.7	-203.0	-191.1	-125.9
	O	-232.9	-200.2	-222.9	-206.0	-225.1
Mean absolute deviation		22.5	14.7	17.0	14.5	
Mean deviation		-19.2	-5.2	-11.2	-4.8	
Mean LMF, \bar{a}_0^d		0.281	0.469	0.301	0.399	

^aThe thermochemically optimum value of λ (that provides the minimum mean absolute deviation of the calculated atomization energies of 55 molecules from the G2-1 set from the experimental values).

^bThe optimum λ value for the tabulated chemical screening constants.

^cSee Note "b" to Table 2.

^dCalculated by (86) and averaged over 22 molecules from the table.

in other words, \bar{a}_0 is the local mixing function averaged over the electron density (it can readily be seen that for global hybrids, calculation of \bar{a}_0 leads, in a trivial way, to the a_0 constant). The mean LMF values listed in Table 4 are the values of \bar{a}_0 averaged over the set of 22 molecules under study. Evidently, the *difference* between two optimum averaged values of exact exchange admixtures (for thermochemistry, on the one hand, and magnetic resonance parameters, on the other) is much smaller for local hybrids (0.1-0.2) compared with the corresponding difference between the a_0 parameters for global hybrids (0.3-0.4) (cf. Tables 4 and 2). This circumstance indicates that the local hybrids are “more universal” functionals (see above). Therefore, the *s*-LMF is also advantageous over the *t*-LMF (the differences between \bar{a}_0 are 0.10 and 0.19, respectively).

To summarize, we note that the thermochemical properties calculated with the use of the local hybrid functionals are virtually the same both in the self-consistent calculations with the LLH potentials and non-self-consistent calculations with the orbitals obtained within the framework of the local density approximation (post-LDA) [119]. This is further evidence in favor of the overall sensitivity of the total energy of the molecule to the fine details of its electronic structure.

CONCLUSIONS

The exchange correlation hybrid functionals with an exact (Hartree–Fock) exchange energy admixture are a powerful tool for solving various problems within the framework of modern density functional theory. Apart from giving excellent results in computational thermochemistry, the hybrid functionals are absolutely indispensable in calculating the “subtler” properties that are sensitive to details of electron density distribution (e.g., the chemical screening constants and electronic *g* tensors). In recent years, the hybrid functional concept received a strong impetus in view of the appearance of the local hybrid functionals in which the exact exchange admixture was introduced by a nontraditional method (in the form of a nontrivial space coordinates function and not in the form of a constant). Moreover, the construction of the localized potentials from the traditional nonlocal hybrid potentials (operators) ensured higher accuracy of calculation of nonthermochemical properties. Recently, synthesis of two concepts, namely, the “local hybrid functional” and the “localized hybrid functional” gave rise to the *localized local hybrid potentials*, which, according to test calculations, proved very promising for a wide spectrum of molecular properties. Today the direction associated with the search for more perfect local hybrid functionals is being actively developed.

It should be noted that here we *did not adhere to* the very popular (but not perfect) classification of the exchange correlation functionals in terms of the “steps” [134] of the “Jacob’s ladder to the heaven of chemical accuracy” [135, 136]. Moreover, we did not discuss the new, rather complex functionals from the “hyper-GGA” category, one of the ingredients of which is also the exact exchange energy density.

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